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J. B. WHITEHEAD, CHAIRMAN
JOHNS HOPKINS UNIVERSITY, BALTIMORE, MD.

THE NATURE OF A GAS

BY THE SAME AUTHOR

FUNDAMENTALS OF
ELECTRICITY AND MAGNETISM

A mathematical approach to the subject of electricity and magnetism, facilitating its practical application to engineering problems. With a historical survey, and a chapter on the physical basis of thermionics and photoelectric phenomena. 432 pages, 6 by 9. 187 figures. 154 problems. Cloth.

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THE NATURE OF A GAS

BY

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FOREWORD

THIS volume is the first of a series of monographs to be published under the auspices of the Committee on Electrical Insulation of the Division of Engineering and Industrial Research, National Research Council.

The Committee on Electrical Insulation concerns itself with all matters bearing on the theory, the experimental study, and the performance of dielectric materials as utilized for electrical insulation. An important phase of the work of the Committee is the establishment through its Sub-committees on Chemistry and Physics of contacts with research in these important fields in its relation to the problems of dielectric behavior, as found in the manifold and complex forms of present day electrical insulation.

Professor Loeb has been one of the first to respond to the efforts of the Committee to assemble a series of authoritative reviews on important fundamental properties of dielectric substances. Gases are utilized as insulators and occur in insulating materials in a wide variety of conditions. Professor Loeb's interesting and logical development of the nature and electric properties of a gas meets an important need and will be gratefully received by students and engineers who are concerned with the problems of the behavior of dielectrics as insulation.

J. B. WHITEHEAD, Chairman.

THE JOHNS HOPKINS UNIVERSITY
January 13, 1931

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LEONARD B. LOEB.

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CONTENTS

CHAPTER		PAGE
I. INTRODUCTION.....		1
1. Historical		1
2. The Units of Electricity.....		4
(a) General.....		4
(b) The Electron.....		4
(c) Occurrence of the Electrons.....		8
(d) The Proton.....		8
3. The Atomic Nuclei.....		10
4. Structure of the Nucleus.....		11
5. The Extranuclear Structure of the Atom.....		16
6. Molecular Structure.....		41
II. THE KINETIC PICTURE OF A GAS.....		57
7. The Avogadro Number.....		57
8. Joule's Law.....		59
9. Equipartition of Energy.....		62
10. Mean Free Path.....		63
11. Molecular Velocities.....		71
12. The Law of Equipartition of Energy.....		78
13. Summary.....		91
III. IONIZATION PHENOMENA.....		98
14. General Considerations.....		98
15. Critical Potentials.....		102
16. Multiple Ionization, or Ionization and Excitation.....		104
17. Mechanism of Ionization.....		106
18. Probabilities of Ionization and Excitation.....		110
19. Ionization by Positive Ions and Temperature.....		112
20. Conditions after Excitation or Ionization.....		115
21. Inelastic Impacts of the Second Class.....		116
22. Dissociation of Molecules by Electron Impact.....		120
23. Photoelectric Processes Leading to Ionization in Gases.....		123
24. Sources of Ionization in Gases.....		127

CONTENTS

APPENDICES

APPENDIX	PAGE
I. Radii of Molecules Determined by Various Methods.....	129
II. Molecular Velocities, Mean Free Paths and Diameters.....	131
III. Conversion Factors and Relations.....	132
IV. General References and Texts.....	135

TABLES

TABLES

1. Periodic Chart of the Atoms.....	27
2. Bohr's Table of the Atoms.....	32
3. Table of Critical Potentials in Volts.....	105
INDEX OF NAMES.....	137
SUBJECT INDEX.....	139

THE NATURE OF A GAS

I. INTRODUCTION

1. Historical.—The discoveries of the early chemists (4 Chapters 1 and 2)*, especially Dalton, following the work of Lavoisier (in 1774–1794) had given rise to the notion that matter was composed of elementary units of substances named after the Greek terminology atoms. Gay-Lussac's investigations of the gas laws and his subsequent quantitative study of gaseous reactions led him to postulate that the gases were composed of *atoms* in a more dispersed state than that encountered in the liquids and solids investigated by Dalton. Certain discrepancies in these results pointed out by Dalton, however, led to the disregard of this assumption and it remained for Avogadro, through his famous rule, really to interpret the nature of a gas in a proper fashion in 1811. Avogadro postulated that while a gas could be made up of separate elementary units, the so-called atoms, this need not always be the case and he showed that the gases studied by Gay-Lussac were in all probability not composed of single atoms but of units consisting of groups of atoms, now called *molecules*, bound together by chemical forces. From the results of Gay-Lussac it appeared that these molecules could be composed of but few atoms (2 in the cases of hydrogen, oxygen and nitrogen) following the well-known laws of

* In Appendix IV, references are given to texts and papers. References to texts are numbered serially 1, 2, 3, 4, etc. References to papers are also numbered serially, but these numbers are always preceded by the capital letter R. These references are included within parentheses; e.g., the expression (4 Chapters 1 and 2) signifies reference No. 4, Chapters 1 and 2 or F. K. Richtmyer's Introduction to Modern Physics Chapters 1 and 2.

Dalton. Avogadro further postulated, as Gay-Lussac had done with his atoms, that in such a molecular gas the same volumes of gases at equal temperatures and pressures must contain equal numbers of molecules. The chemical evidence at this time, however, was too scanty to permit the acceptance of these views with certain *apparent* contradictions encountered. It was, accordingly, not before 1865, when, through the systematic development of organic chemistry, the work of Dumas on vapor densities, and the law of Dulong and Petit concerning specific heats, that the hypothesis was accepted.

In the meantime the work of Joule had established the mechanical equivalent of heat and shown the mechanical nature of heat, while Mayer and Helmholtz had enunciated the law of the conservation of energy, so that by 1850 the stage was set for a plausible explanation of the gaseous state in the form of a molecular or better kinetic theory of gases. In fact, in 1851 Joule (10 Chapter 1) showed that the pressure of a gas could be accounted for by the bombardment of the walls by gas molecules, in terms of the expression $p = (1/3)Nm c^2$, where p is the pressure of the gas, N the number of molecules per unit volume, m the mass of a single molecule, and c an average velocity of motion of the molecules of a special type. Nearly 100 years earlier Daniel Bernoulli had deduced the same law on an entirely hypothetical basis.

In 1857 the great mathematical genius Clausius (who had antedated Kelvin in enunciating the second law of Thermodynamics) overcame the great objection to Joule's kinetic theory by his concept of the "mean free path" of the gas molecules, i.e., the average distance covered by the molecules between impacts. From then on the concept of the gas as consisting of enormous numbers of small units composed of a few atoms each, in constant heat motion, has developed and gained in precision and certitude.

During the last twenty years, the work of Perrin

(R 17) in *quantitatively demonstrating the reality of heat motions of molecules* in 1908, the measurement of the number of molecules in a cm^3 by at least seven independent methods, and the direct observation of the magnitudes and distribution of molecular velocities and free paths, have justified the theory beyond the shadow of a doubt.

In order, therefore, to understand the nature of a gas, so that we may study its electrical behavior, we must investigate first the nature of the atoms and molecules, as units, and then organize these structures, in their complex behavior, into a whole, comprising in its properties the condition of matter termed the gaseous state. In doing this it will be necessary for the sake of brevity to forego an historical or experimental analysis of the progress of the investigations during the last fifty years which led to our knowledge, and to state, in a clear and consistent form, merely the concepts and mechanisms to which we have been led by these discoveries. Wherever possible, references to the work which has led to these conclusions will be given, so that those interested may see for themselves just how far the conclusions are justified.

In constructing such a picture of nature, it is far clearer to make the picture concrete by as close a mechanical likeness as possible. It must, however, be realized that in this process *we are entailing a considerable risk of being too dogmatic, somewhat inaccurate, and exceeding distinctly the real scope of our actual scientific knowledge* (16 and 11). Thus while we are justified, for the sake of clarity in a report of this type, in the mode of procedure chosen, we must openly recognize the chances we are taking, and not pursue our analogies too far. The danger mentioned above is being brought home to physicists with exceptional emphasis in these days of relativity, quantum theory, and wave mechanics, especially in the very fields of atomic structure which we are about to invade. Thus, for instance, the very mechanical ether of four decades ago has been replaced by the elegant and accurate equa-

tions of relativity, while the spherical volume of negative electricity of some 10^{-13} cm diameter (which depicted the negative electron of twenty years ago) is now replaced by certain characteristic mathematical functions (11) varying with the state of the electron, whose form most resembles a complex superposition of a series of interfering electromagnetic waves of infinite extent. This description of the electron in terms of equations whose mechanical interpretation is as yet well-nigh impossible, results from the new wave mechanics, whose adequacy is each day being established more and more surely, both by the ability to correlate otherwise incompatible phenomena and in such experiments as the electron reflection and scattering experiments of Davisson and Germer (R 1), G. P. Thomson (R 2), and O. Stern (R 3 and 5 Chapter 21).

Having, therefore, agreed to a mode of procedure, and recognizing its hazards, we may now turn to the study of atomic, molecular, and gaseous structure.

2. The Units of Electricity. (a) *General*.—Ultimately in describing all matter we must come down to electricity. Scientific investigations, so far, indicate that all matter is made up of atoms of some 92 elements which, in turn, are built up of electrical units (1, 2, 3, 4, 6, 20). Of the *ultimate nature* of electricity we are in complete ignorance, and we can only *describe the form in which it appears in our physical experiments*. These indicate that there are apparently two electrical units or entities, named in accord with Franklin's original one fluid theory of electricity, the positive and negative electricities. Though Franklin's one fluid theory is, in general, in error (electricity is particulate and both signs of electricity flow under appropriate conditions), the names given by Franklin have become fixed and we shall use them.

(b) *The Electron*.—The negative unit of electricity called hereafter the *electron* (2, 3, 4, 7), when it appears independent of matter, has a mass (or inertia) about (1/1850) that of the hydrogen atom; the mass of an elec-

tron is 8.99×10^{-28} gram, when at rest.* It carries a charge of 4.77×10^{-10} absolute electrostatic units or 1.59×10^{-19} coulomb. Its charge has been measured when it is relatively at rest on the surface of a material particle (7), and its mass has been studied and the ratio of charge to mass determined (R 3, 4) for velocities ranging from those of some 10^7 cm per second to velocities reaching to 0.99 the velocity of light, or nearly 3×10^{10} cm per second. As its velocity increases, the mass of the electron appears to increase according to the theory of relativity (and within the limits of precision of measurement) in the following manner:

$$m_v = m_0/[1 - (v^2/c^2)]^{1/2} \quad (1)$$

In this equation m_v is the mass at a velocity v , m_0 is the mass at rest or 8.99×10^{-28} gram, and c is the velocity of light. Thus, in this respect the electronic mass behaves in accord with the restricted theory of relativity deduced for a material particle.

As to the "physical size" of the electron, the facts are much more obscure, and depend on the particular interpretation to be placed on the word "size." Since an electron has an electrical field about it supposedly extending to infinity, it will react on another electron placed at a distance r from it with a force f , which according to Coulomb's law, is:

$$f = e^2/r^2 \quad (2)$$

If we judge the size of an electron by some sort of a physical effect, say a change in its motion or its state in an atom, the "size" of the electron and its reacting partner (in this regard) are determined by the *greatest value of r at which the effect is produced*, i.e., the value of r when the force is great enough just to produce the change observed. Thus, for example, while in ordinary encount-

* For other numerical constants see Appendix III.

ers or collisions the diameters of molecules or atoms having electrons are some 10^{-8} cm, there are "encounters" between "activated" atoms and molecules which produce changes (such as light emission) at distances of 10^{-4} cm as a result of the action of the electrical and electromagnetic forces of the electrons in the two configurations. In this sense, then, the size of an electron can be defined only in terms of a given effect observed. In some cases this even reduces to meaning that the definition of "size" depends on the limits of experimental certainty at which the effects produced at different distances can be detected. Obviously, then, such a criterion must depend on the delicacy of the tests and apparatus involved, as well as on the particular phenomenon used as a criterion.

On the other hand, classical electrodynamics *enabled us to fix the size of the electron as the size of a sphere of negative electricity which would have an electromagnetic inertia equal to that of the electron* (R 5). This law says that:

$$m = (2/3)(e^2/a) \quad (3)$$

where m is the mass or inertia, e the charge, and a the radius of the sphere. When calculated out, this gives the electron a radius of some 2×10^{-13} cm. Fixing a radius in this fashion is equivalent to saying that the Coulomb inverse square law of force applies to two electrons placed apart from each other at distances varying from infinity to 2×10^{-13} cm, and that for distances shorter than 2×10^{-13} the law changes perhaps abruptly to some other law. Actually no direct experimental evidence on this point applies to the electron. If, however, the classical equation were correct, then the unit of *positive* electricity should be about (1/1850) of the electron in diameter, and the nuclei, or the inner structures of atoms containing both electrons and positive units, should have a diameter of the order of magnitude of the electron. The experiments on the scattering of helium nuclei and unit positive charges by Rutherford (R 6) and his pupils defi-

nitely indicate that for the simpler nuclei such as that of the helium atom the nuclei do approach to some 7×10^{-13} cm of each other (i.e., have diameters of the order of 7.0×10^{-13} cm) before the scattering deviates seriously from that predicted by the inverse square law.

Now classical electrodynamics has been found to fail in atomic phenomena, and we must thus proceed with caution. On the more accurate and modern interpretation of the electron in *terms of a characteristic equation*, which closely predicts the behavior of an electron, it is doubtful whether the above mechanical interpretation is correct. It is probable, however, that when the wave mechanical electron is translated into as near a mechanical picture as possible, the equivalent of the physical dimensions which would produce the same effects would lead to the same general order of magnitude as that given above. We can thus assume that the electron as we choose to consider it is a minute body as compared with the dimensions of the atom.

In addition, recent experimental and theoretical advances attribute to the electron still one more property of immense theoretical importance in the combinations of electrons into the structures of atoms and molecules and the stability of these structures. This is again a mathematical property which amounts as nearly as can be stated to an electron *spin* and results in giving to an electron a weak but definite magnetic moment. The nature of this moment (R 7) is calculated from the expression:

$$\mu = (eh)/(4\pi mc) \quad (4)$$

where e is the charge on the electron, m its mass, c the velocity of light, and h the Planck constant of quantum action. This leads to a value of μ equal to 2.7×10^{-35} . It appears to be of great importance in questions of stability whether two electrons have a spin in the same sense or in opposite senses, and the pairing of electrons in so many

chemical reactions seems to be determined by the fact that they have spins in opposite senses.

(c) *Occurrence of the Electrons.*—Inside the atoms electrons appear in two separate régimes:

(1) In the nuclei of the atoms bound by forces involving tremendous energies if they are to be liberated (1, 2, 6).

(2) In groups or levels in the outer structures of the atoms and molecules (1, 2, 4, 5, 6).

Any process capable of tearing electrons out of either nuclei or outer structures will lead to the presence of temporarily free electrons. Hence the spontaneous explosions of the nuclei of radioactive atoms in the act of transformation liberate electrons, and any catastrophes imparting enough energy to the outer electrons of the atoms to remove them from the atoms will liberate electrons. Such agencies are X-rays, light waves, rapidly moving charged particles (such as other electrons or charged atoms) and the impacts due to heat motions of molecules. Electrons do not remain free very long (10 Chapter 11), except in certain gases when very pure or in good vacua. They either attach themselves to molecules of impurity or diffuse to the walls of the container and ultimately reach some atom deficient in electrons. In metals it seems probable that the electrons can remain free within the metal under somewhat peculiar conditions, which render the metals such good conductors. To remove the electrons from the metal requires, however, an appropriate amount of work (R 8).

(d) *The Proton.*—The second electrical entity is the unit of positive electrical charge. It was early found that all the smallest positively charged bodies had the mass appropriate to atoms or molecules (2, 3, 19). Of these the lightest was the *nucleus of the hydrogen atom* after the one electron present had been removed from such an atom. The more recent knowledge of the electrical relationships of the atoms and the fact that in the artificial

disintegrations of nuclei of light elements the hydrogen nucleus is emitted, has led to the conclusion that the *nucleus of the hydrogen atom is the unit of positive electricity*. It is called the *proton*. It carries the charge of the hydrogen ion in electrolysis, i.e., 4.77×10^{-10} positive absolute electrostatic units of electricity, a charge exactly equal in magnitude but opposite in sign to the electron. Its mass is closely that of the hydrogen atom, or 1.662×10^{-24} gram (22). It is assumed that, as with the electron, its mass varies with velocity according to the predictions of relativity (see Eq. 1). Its dimensions, as discussed under the case of the electron, are very minute if its mass is entirely electromagnetic in character as calculated by classical electrodynamics. Thus, on these assumptions, the radius of the proton is of the order of 1×10^{-16} cm.

It is probable that the proton, like the electron, has a spin and a magnetic moment in view of certain conditions of stability in the nucleus; this view is now definitely confirmed by the discovery of the ortho and para hydrogen molecules in spectroscopic investigations (R 9).

The proton appears isolated only for intervals of time over which it has velocities sufficient to prevent its picking up an electron to form a neutral hydrogen atom. It appears in all discharge phenomena in which hydrogen gas is present under conditions where the electrons can be knocked loose from the atoms or molecules (R 10). It also very, very rarely appears when, by chance, a light atomic nucleus is disrupted by the bombardment with an α particle from a radioactive change (2 p. 73 ff.). It is known that the proton is able to exist in a free form temporarily in a metal like palladium which dissolves hydrogen in large quantities and is porous to it.

The essential points to be remembered about the proton are that it carries a positive charge equal and opposite in sign to that of the electron; that it has a mass 1850 times that of the electron; and that as far as we know its dimensions are minute even compared to an electron.

3. The Atomic Nuclei. It is out of these two entities, the proton and the electron, that all matter appears to be built. While it was early recognized that most of the mass and the positive charge were definitely associated in the remnants of atoms which had been influenced in one way or another by having electrons removed, the nature and localization of the positive charge were not definitely known. By bombarding the atoms of matter with the α particles from radium (helium atoms with a double positive charge, moving at velocities of from 2×10^8 to 2×10^9 cm per second), Rutherford and his pupils showed conclusively that the positive charge in all atoms resided in a small fraction of the volume occupied by the atom or molecule as a whole (1, 2 p. 10 ff.). In fact, the scattering of these α particles by thin foils of gold, silver, copper, or aluminum indicated that the particles were deflected by what were nearly positive point charges, acting on the positively charged α particles according to Coulomb's inverse square law of repulsion. It was only when the α particles came within 5×10^{-12} cm or less of the center of the atoms of gold that the scattering of the α particles began to deviate appreciably from the inverse square law (2). For lighter atoms the approach was closer, but was never less than some 7×10^{-13} cm. This led Rutherford to postulate the *nuclear atom*, that is, an atom built on the lines of a miniature solar system, the *massive positive charge occupying a minute region in the center of the atom* as compared to the space occupied by the rest of the atom. Between this positive sun or *nucleus* and any other charges (either electrons or α particles) the electrical forces were those obeying the well-known Coulomb law:

$$f = Ee/r^2 \quad (5)$$

where f is the force of attraction or repulsion;

E is the charge on the α particle;

e is the charge on the electron;

r is the distance between e and E .

In these encounters it turned out that the mass of the nucleus was practically that appropriate to the atomic weight of the atom, or more exactly $1.657 \times 10^{-24} \times A$ gram, where A is the atomic weight on the basis of oxygen 16.000.

At the time of his experiments Rutherford estimated Z , the positive charge on a nucleus, as approximately one-half the atomic weight A . Very shortly thereafter results from radioactivity and the analysis of the X-ray spectra of the elements in the periodic table led Rutherford's pupil Moseley to conclude that the *charge on the nucleus was the charge on the proton multiplied by the serial number of the element in Mendeleeff's Periodic Table of the elements, as given in the modern chemical tables* (1, 2, p. 47 ff, 6). This view has been completely substantiated by modern investigations, so that today we know (see Table I) that the gold nucleus has 79 times the positive charge on the proton, the silver nucleus has 47 times the charge on the proton, the copper nucleus has 29 times the charge on the proton, the aluminum nucleus has 13 times the charge on the proton, and so on. Hence the general picture of a neutral atom of diameter some 2×10^{-8} cm consists of an extremely small nucleus (diameter some 10^{-12} cm) having 99.98 per cent or more of the mass of the atom concentrated in it, carrying a positive charge equal to its number in the periodic table, and surrounded in some way by a swarm of external satellites (*electrons*) equal in number to the charge on the nucleus.

4. Structure of the Nucleus.—With this picture before us we may look with some care to the nature and structure of this minute nucleus (2). In spite of its minute size and relative inaccessibility we have obtained a surprising amount of knowledge concerning it, thanks largely to radioactivity and the genius of Rutherford.

Next to the "size" and charge of the nucleus, perhaps the most important feature is its stability. All the early attempts of the alchemists to transmute elements failed

because of this very fact. To date no external physical agency known to man, except that coming from disrupting radioactive nuclei which are beyond our immediate control, have been able to affect the stability of atomic nuclei. Anderson's temperatures of $20,000^{\circ}$ C (R 11) in exploding wires and Millikan's 750,000 volt X-rays (R 12), to say nothing of lesser agencies, have been unable to influence atomic nuclei. Except for an occasional encounter of a nucleus with an α particle having an energy corresponding to free fall through a potential of from 2 to 5 million volts, there have been no changes observed in our atomic nuclei by external physical agencies. Hence we must conclude that nuclei of all the known elements possess a stability which would require bombardment by particles endowed with more than the above amount of energy or perhaps temperatures of 2.2×10^{10} degrees C, to cause disruption. This extraordinary stability must be borne in mind in view of the fact that these minute nuclei are themselves structures which contain electrons and protons bound together, but segregated from the *extranuclear* electrons by an *energy wall* of very high magnitude.

That in truth our atomic nuclei are complexes of (a) protons, (b) electrons, and (c) particularly stable configurations of electrons and protons, called the α particle, follows from radioactivity (2, 6). Among our known elements are a certain number having atomic weights exceeding that of lead (206 to 208), and having atomic numbers (positive nuclear charges) ranging from 82 to 92, which are so complex that in the environment of the surface of our earth they *spontaneously* become unstable. It is possible that perhaps some other of our atomic nuclei are also unstable, but except for potassium and rubidium the stability is so great that the disruption cannot be detected with certainty. These unstable nuclei break up with the emission of charged particles of matter initially termed α rays and β rays. Rutherford (R 13) by a brilliant series of experiments proved that the α particles (or rays) are

merely doubly charged atoms of helium. Since helium is the second element in the periodic table, its nuclear charge is double that of the proton and it has two orbital electrons; hence, an α particle is a helium nucleus projected from a disintegrating atom with a velocity from 2×10^8 to 2×10^9 cm/sec. The β rays (or particles) were found to be electrons traveling with all velocities ranging from 10^8 to 2.9×10^{10} cm per second. The nuclear origin of these rays is attested by the fact that the *loss of an α particle (2 positive charges) reduces the atomic number of the parent atom by two units, while the loss of a β ray (gain of 1 positive charge by loss of an electron) increases the atomic number by one unit without changing its mass appreciably* (2, 19). A further constituent of the nucleus is discovered in the rare encounters when a fast α particle crashes into the nucleus of a light atom such as Al or N. In the case of N the α particle sticks in the nucleus (2). In all cases observed, a proton is shot out with a high velocity, sometimes having an energy greater than the energy of the incident α particle. In the case of N the nuclear mass is increased by 4 atomic weight units and decreased by 1 such unit (gain of 1 helium nucleus and loss of 1 proton); its charge is increased by 1 positive unit. In the case of N (nuclear charge 7) it leads to an element of atomic weight 17 and a nuclear charge 8 (identical with O). Very recently oxygen of atomic weight 17 has been observed present in our atmosphere to the extent of one part in 10,000. So we see that the nuclei contain α particles, electrons, and protons (R 14).

How the α particles, protons, and electrons are packed together in a minute nucleus it is hard to understand, but that they are is a fact. It seems likely that most of the charges are in the nucleus as α particles (helium nuclei of mass 4 and charge 2), with a few protons and enough electrons so as to make up the atomic charge equal to the atomic number. A certain number of α particles are packed in the nucleus with two electrons closely associ-

ated with them (the so-called α' groupings) (2). These add to the mass of the nucleus without adding to the charge, and they are evidenced especially in the radioactively unstable nuclei.

The α particle or helium nucleus itself is a complex grouping of electrons and protons of apparently exceptionally great stability. In this configuration its mass 4 comes from 4 protons and its charge of 2 positive units from the fact that two electrons neutralize the charge of 2 of the protons. In the formation of this substance from protons a peculiar fact comes to light. The mass of a proton is 1.0077 atomic weight units on the scale of oxygen 16.000. The weight of 4 protons in the free state is 4.031 such units. On the other hand, helium with 4 protons and 2 electrons has a mass of 4.000 atomic weight units. Hence the "*packing*" (R 15) of the protons with 2 electrons in the helium nucleus (or α particle) due to the "*overlapping*" of the electromagnetic fields results in the annihilation of 0.031 atomic weight units of mass. This last mass is supposed to go off as radiation whose energy equivalent, $m = E/c^2$, is given by the theory of relativity. Here m is the mass in grams, E is the energy in ergs and c is the velocity of light in cm per sec. Thus the loss in mass is equivalent to 4.5×10^{-5} ergs of energy. Since this enormous energy is given off in the formation of helium nuclei, *the same energy must be put back into the nucleus to disrupt it* so that the stability of that nucleus is not surprising, for we do not command energy sources today with which we can put as much as 4.5×10^{-5} ergs into a single α particle at once.* The values of the "*mass defect*" of other atomic nuclei (nuclear charge Z times 1.0077 less the observed atomic weight) have as yet not been accurately observed, owing to uncertainties in the exact values of the atomic weights for various atoms due to causes to be discussed. Hence we can only infer that a "*packing effect*" of at least this

* The energy of the fastest α particle is about 1.4×10^{-5} ergs.

order of magnitude enters into each nucleus for every α particle contained, and possibly more. The stability of nuclei is therefore at least comprehensible, although we know nothing of the process by which the charges are packed together.

The peculiar structure of nuclei, based on combinations of masses 4 with 2 positive charges, masses 1 with 1 positive charge, and electrons of relatively negligible mass with 1 negative charge, leads at once to another important fact. It enables us to imagine nuclei as being built up so as to have a given positive charge but *any number of masses* (2, 5, 6, 19, 20). Thus oxygen of atomic number $Z = 8$, and 8 charges on its nucleus, could be made up of 4 α particles having a mass 16 and 2 charges each. It could also be composed of 4 α particles and a proton making a mass 17, with 1 electron giving a charge of 8, and again it could be made up of 4 α particles and two protons giving a mass 18 with 2 electrons to give it a charge of 8. Such elements, having several masses and the same nuclear charge (which means, as we shall see, identical chemical properties), are called *isotopes*. Until lately oxygen and carbon were believed to have no isotopes. Recent spectroscopic data, however, have shown conclusively from the moments of inertia of oxygen molecules that all three isotopes of oxygen, above listed, occur in the atmosphere, and carbon has also been found to have isotopes. It seems now probable that all chemical elements as we isolate them are mixtures of atoms of several atomic weights but having the *same nuclear charge* (isotopes), some of which may of course be relatively rare. Thus the atomic weights as listed in the tables are but the weighted averages of several kinds of atoms of different atomic weights of identical chemical properties, present in different amounts. For example, neon, the first isotopic element observed directly by J. J. Thomson in the mass spectrograph, has an atomic weight of 20.2. It consists of two chemically inseparable neons of atomic weight 20 and 22, present in

the ratio of 10 to 1. The atomic weight of chlorine, 35.45, is due to two chlorines whose nuclei are built up differently but have the same charge, and atomic weights 35 and 37. In the radioactive series of elements with atomic numbers from 82 to 92 some elements have at least 6 or more isotopic forms. There are now recognized two kinds of lead from uranium and thorium minerals, having identical chemical properties but atomic weights of 206 and 208, respectively, so that our common commercial lead of atomic weight 207 is merely a mixture of the two leads.

From all the foregoing we have learned that an atom consists first of a nucleus of minute dimensions (10^{-12} cm), carrying the greater portion of the mass of the atom and having a positive charge Z characteristic of its numbered position in the periodic table, which accordingly gives it its chemical properties. The positive nuclear charge is then the *number* of the element in the periodic table. This nucleus is a complex of helium nuclei (α particles), protons and electrons, bound together probably with a loss of mass due to radiation and hence very stable, requiring enormous energies to disrupt it and thus electrically quite distinct from the outer electrons of an atom which make the atom electrically neutral. Since the same charge can be achieved by different combinations of α particles, protons, and electrons (which combinations, owing to the small mass of the electron, give several different masses for the same charge) we are led to expect the existence of isotopes. These have now been observed in the case of most elements.

5. The Extranuclear Structure of the Atom.—Having thus analyzed the cores of the atoms, we can now turn to the external electronic structure to see how the charge on the nucleus gives the atoms their diverse chemical properties.

As, under usual conditions, matter is electrically neutral, it is to be expected that our atoms of matter in general must be electrically neutral configurations, and this

belief is borne out by observation. In fact, there are two tendencies in atomic behavior: the one is a striving for a dynamical stability depending on the arrangement of the electrons about the nuclei in certain apparently preferential and stable configurations; the other is a striving after electrical stability, i.e., electrical neutrality.

These two tendencies govern the whole general behavior of the atoms and molecules, including their chemical properties. While in general both types of stability are fulfilled, there are cases where dynamical stability and electrical neutrality conflict; thus we see dynamical stability achieved at the expense of electrical neutrality in the polar compounds, and also in ions in solution.

Since we recognize these two types of stability, it is our next task to study what such stability implies. The meaning of electrical stability or neutrality in an atom or molecule is perfectly clear. It merely signifies equality of the positive charges manifested by the nuclei of the atoms and molecules and the number of *extranuclear* electrons surrounding the atoms or molecules. Thus at once if we have the nucleus belonging to an atom whose position in the periodic system is represented by the number Z , for example 10, we know it has Z , i.e., 10, positive charges in its minute nucleus; to be neutral, it must have at least 10 electrons in an external swarm about the nucleus. If it is a molecule composed, say, of an atom of nuclear charge 9 combined with an atom of nuclear charge 11, the compound must have 20 electrons surrounding the two positive nuclei, which are in general separated by distances of the order of 10^{-9} to 10^{-8} cm. Thus all that electrical stability (neutrality) tells us is that if we take the Z th element in the periodic table it has a nuclear charge of Z positive units (equivalent to that of Z protons), and is surrounded by Z external electrons. In a molecule it means that the sum of the nuclear charges Z of the components must equal the number of electrons present. This fact greatly simplifies the analysis of the problem, in that

it gives the number of charges present uniquely and enables us to turn our attention to the arrangement of the electrons.

The next question which one might properly ask is how the Z electrons are arranged about the nucleus. First, whether they are in motion or at rest; secondly, if in motion or at rest how are they arranged? In answer to this question we can reply that we appear to know an amazing amount in one sense and yet absolutely nothing in another sense. The fact is that it was in a study of atomic structure that we first learned that our whole system of classical electrodynamics, formulated by Maxwell, ceased to apply, so that having no mechanical precedent from our known physical world to apply to the situation we have had to improvise an empirical system of relations which is quite formal, and mechanically inexplicable, but has been crowned with uncanny success.

The facts are as follows: It is a well-known mathematical physical theorem that a group of point charges acting under an inverse square law of attraction (Coulomb's law) cannot be in stable equilibrium unless the components of the group are in relative motion. For example, our solar system retains its stability solely as a result of the motions of the planets. The same type of law of attraction holds for the swarm of Z electrons about a minute massive nucleus of charge $+Z$. Thus, much as chemists of the past decade desired it, there was no way of building up a nuclear atom with stationary electrons. We must then endow our electrons, whatever they are, with the equivalent of a motion about the nucleus in some sort of orbits in formal analogy with the mechanics of our solar system. If we do this we find at once that the electrons must describe elliptical or circular orbits about the nucleus. The size and shape of such orbits are at once fixed by the size of the attractive force $(Ze)e/r^2$ (where Ze is the nuclear charge, e the electron charge, and r the instantaneous distance), and the velocity and mass of the electron which determine its centrifugal force at the point in question,

that is, mv^2/r , where v is the linear velocity, m the electronic mass (nucleus considered essentially stationary), and r again the instantaneous value of the radius of the orbit or the distance r between nucleus and electron. It is at once seen that for any given values of Ze and m , the values of r will depend on the values of v chosen, so that since the electron may have any velocity v it will have an infinity of possible orbits. This need not alarm one, however, except that another fact must be considered. An electron executing an orbit about a nucleus is by the use of the very relations cited above continually accelerated towards the nucleus, as is the case of all orbital motion under central forces of this type. But according to the classical electrodynamics of Maxwell such an *accelerated moving charge must radiate energy*. If then the electron is obeying Maxwell's laws in this case, its kinetic energy $(1/2)mv^2$ is continually being utilized in electromagnetic radiation, and must be replenished at the expense of its potential energy. Hence ultimately all electrons should radiate energy at the expense of their potential energy and so eventually fall into the nucleus, thus annihilating the atoms. This contradicts our experience, for atoms are quite stable and apparently do not disappear. Accordingly, either our assumed electronic motion is wrong though based on an inviolable principle, or our classical dynamics is wrong, or we cannot treat an electron as a planet moving in an orbit about the nucleus. In view of our complete ignorance of how to treat the electron in an atom without violating either of the principles above, Bohr made an assumption which permitted our retaining the planetary analogy so as to guide our thinking, but which at the same time enabled us to make formal calculations of the electronic behavior in terms of the energy relations involved, without violating any fundamental physical principles. In other words, Bohr's postulates are such that while we may think in terms of an analogy to a circulating electron in applying the postulates, the postu-

lates in reality constitute the conditions to be fulfilled by some as yet unknown atomic process in order to produce spectroscopic and other data as observed. Accordingly, while in what follows we shall speak of electron orbits and shells of electrons, etc., we must realize that the electrons may not appear in any such a form in the atom. This merely signifies that, as in so many other places in physics today, we are forced to describe phenomena accurately only by equations or mathematical forms of representation for which unfortunately we have no close gross mechanical analogy.

Bohr's postulates are elaborated in the following five points with the necessary interpretation (2 p. 184).

1. The electrons move in orbits (at first these were assumed circular but later elliptic) about the nucleus.

2. The electrons cannot take any one of the infinite number of possible orbits about the nucleus as a stable orbit but only a very few discrete orbits governed by special conditions. That is, since the Coulomb force between nucleus and electron, Ze^2/r^2 , must equal the centrifugal force, mv^2/r , we can write:

$$(Ze^2/r^2) = (mv^2/r) \quad (6)$$

or:

$$(Ze^2/r) = mv^2 \quad (7)$$

As v and r are unrestricted, an electron should be able to take any orbit as stated above. Bohr postulates that the electron can only be in stable equilibrium in certain definite orbits of radii r_1, r_2, r_3 , etc., to be defined.

3. To define the restricted orbits Bohr postulates that contrary to classical electrodynamics *there are certain orbits in which the electron does not radiate energy*. While there is a real contradiction between classical electrodynamics and Bohr's assumptions if we mean by this *real electron orbits* about a nucleus which do not radiate energy, there is no contradiction if we say that there are

certain conditions of the electrons in the atom (governed by the newly established quantum laws) which for convenience we shall term orbits, or better energy states, in which the electron does not radiate energy. This interpretation of Bohr's original terminology is really more correct in the light of modern advance in wave mechanics.

4. To describe the restricted orbits, Bohr postulated that these were characterized by the total energy of the electron in the orbit. Thus in a stable orbit of radius r_1 the total energy E_1 characterizing this orbit is given by:*

$$E_1 = -\frac{1}{2}(Ze^2/r_1) \quad (8)$$

The orbit represented by a radius r_2 is characterized by an energy:

$$E_2 = -\frac{1}{2}(Ze^2/r_2) \quad (9)$$

In order to establish a relation between these stable orbits and atomic behavior, Bohr assumed, in conformity with the quantum laws which appear to govern atomic phenomena, that the electrons radiate energy only in going from a stable state of higher energy content, E_2 , to one of lower energy content, E_1 , according to a law which says that:

$$E_2 - E_1 = h\nu \quad (10)$$

Where ν is the frequency of the radiated electromagnetic wave or light emitted, and h is a new constant due to Planck, of value 5.64×10^{-27} erg \times sec. This quantum $h\nu$ we shall find of the greatest importance in all our study of gases and electrical breakdown of gases. Conversely, to raise the electron from an energy E_1 to the higher state E_2 in an atom, we must give it the energy $E_2 - E_1$, either as a quantum of light, $h\nu$, which must be absorbed, or by imparting the necessary energy through a collision with a

* This characterization of the energy in the orbit will become clear later in the discussion.

rapidly moving electron or other electrified body. It is seen at once that this law relates the stable electronic states (which we term orbits for convenience) to the frequency of the light emitted in moving from one orbit to another, and further definitely limits light-emitting processes of *atomic electrons to transitions between these few fixed states.*

5. In an effort to define the orbits, Bohr applied a brilliant restriction, namely, that *only those so-called orbits are stable in an atom for which the moment of momentum, mvr , is equal to whole multiples of the quantity $(h/2\pi)$.* Since h has the dimensions of a moment of momentum (mass times velocity times distance) as well as energy times time, the moment of momentum of the electron in a stable orbit is $(nh/2\pi)$, where n is a whole number: (That is, electrons in stable orbits in an atom must have whole multiples of $(h/2\pi)$ for their moments of momentum).

The above five postulates at once fix the size of the possible orbits for given values of Ze and n and allow certain other important conclusions to be drawn. From the postulate that moment of momentum, mvr must equal $\frac{nh}{2\pi}$, where n is an integer, and from equation (7) it at once follows that,

$$\frac{Ze^2}{r} = \frac{mn^2h^2}{4\pi^2r^2m^2},$$

whence,

$$r = \frac{n^2h^2}{4\pi^2Ze^2m} \quad (11)$$

and

$$v = \frac{2\pi Ze^2}{nh} \quad (12)$$

Hence the radii of, and velocities of the electrons in Bohr's hypothetical stable orbits are fixed by the equations (11) and (12).

By convention the *potential* energies of the electrons in the orbits of radius r are made negative and have a

value $-\frac{Ze^2}{r} = -mv^2$. The kinetic energies of these

same electrons are represented by $+\frac{1}{2}mv^2$. The total energy of an electron of velocity v in an orbit of radius r is then

$$E = -mv^2 + \frac{1}{2}mv^2 = -\frac{1}{2}mv^2 = -\frac{1}{2}\frac{Ze^2}{r}. \quad (13)$$

Substituting the value of the radius r from the equation (11) we at once have,

$$E = -\frac{2\pi^2 m Z^2 e^4}{h^2 n^2} \quad (14)$$

Hence the various stable orbits mentioned under postulate 4, and characterized by equations 8 and 9 can be written as

$$\begin{aligned}
 E_1 &= -2\pi^2 m Z^2 e^4 / h^2 (1/n_1^2) & (a) \\
 E_2 &= -2\pi^2 m Z^2 e^4 / h^2 (1/n_2^2) & (b) \\
 \cdot &\cdot & \\
 \cdot &\cdot & \\
 E_n &= -2\pi^2 m Z^2 e^4 / h^2 (1/n_n^2) & (n)
 \end{aligned} \quad | \quad (15)$$

These equations at once enable us to write the energy difference leading to a radiation of light between orbits characterized by E_1, E_2, E_3 , etc., in terms of Bohr's assumed relation in postulate 4, taking account of the signs involved as

$$h\nu = E_2 - E_1 = - (2\pi^2 m Z^2 e^4 / h^2) \left(\frac{1}{n_2^2} - \frac{1}{n_1^2} \right)$$

$$= (2\pi m Z^2 e^4 / h_2) \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right), \quad (16)$$

or ν the frequency of the light emitted in the transition from an outer orbit r_2 of energy E_2 to an inner orbit r_1 of energy E_1 is given by:

$$\nu = (2\pi^2 m Z^2 e^4 / h^3) [(1/n_1^2) - (1/n_2^2)] \quad (17)$$

It is at once clear that the equation for ν represents a single frequency for the transition from E_1 to E_2 for only one of a set of values of n_1 and n_2 . It is furthermore clear that n_2 must be larger than n_1 and not equal to it, since the expression as a whole must be positive as written. Hence if n_1 and n_2 take on any successive series of values, such as 1, 2, 3, 4 for n_1 , and 2, 3, 4, 5 for n_2 , we see that these can be made to represent a group or series of frequencies which represent assumed electron transitions between energy levels described as E_1 and E_2 . Any pair of values of the integers chosen for n_1 and n_2 in which n_2 is greater than n_1 represent a single transition from the specific level characterized by the numerical value of n_2 to that of n_1 . That n_2 must be greater than n_1 merely means that the orbit characterized by n_2 is at a greater distance from the nucleus (i.e., greater potential energy) than that characterized by n_1 .

Making $n_1 = 2$ and n_2 successively 3, 4, 5, 6, 7, etc., leads to a peculiar type of converging series. This is of great interest, inasmuch as the frequencies of vibration in the bright line spectra observed by Balmer and later Rydberg and others for many atoms were expressed by just such a law. In fact, if we take $n_1 = 2$ and $n_2 = 3, 4, 5$, etc., we obtain nearly the *exact* values of the experimentally obtained frequencies of the Balmer series for hydrogen if we put $Z = 1$ in our equation. In view of the fact that the constant term $2\pi^2 m Z^2 e^4 / h^3$ is a very complex and purely theoretical expression, an agreement of the accuracy limited only by the accuracy of the values of e , h , and m is most significant. If in place of $n_1 = 2$ we had used $n_1 = 1$ and let $n_2 = 2, 3, 4, 5$, etc., we should have found the Lyman series in the ultra-violet for hydro-

gen. By making $n_1 = 3$ and $n_2 = 4, 5, 6$, etc., we should have found the series observed by Brackett in the infrared for hydrogen. If we set $Z = 2$, which is the value for helium, and give n_1 the values 3 and 4, varying n_2 accordingly, we can compute the two series of lines observed by Fowler and Pickering, respectively, in the spectrum of helium.

While numerical coincidences of this type are as a rule capricious, the remarkable number of such relations deduced by appropriately fixing Z and choosing reasonable values of n_1 and n_2 have given us remarkable confidence in this scheme of representation. In later years Bohr and Sommerfeld (2 Chapters 10 and 11) have improved the theory by taking account of the ellipticity of the orbits and correlating the study with the rapidly accumulating data on atomic and molecular structure from the chemical views on stability. On the whole, the mass of evidence of the sort now accumulated has given us complete confidence in the general classification of the phenomena of light emission and the electronic arrangements resulting from this study. Accordingly, while we cannot picture as yet the actual mechanisms occurring in the atom, we can with great accuracy predict the behavior of a given atomic configuration, even before it is discovered.

While the results of the study of spectra have aided a great deal in describing the stable configurations and groupings, these results alone would hardly have sufficed to gain the complete picture, had it not been (a) for the assistance given by the periodic table in showing that certain groups of atoms were dynamically stable in different degrees, and (b) for the correlation of this information with the atomic number (13). Thus it was clear from the close similarities of the K or the L series of X-ray spectra for all the atoms in the periodic table for which they occur, that they represented X-rays from definite electronic groupings (K or L groupings), which must be similar for all atoms. However, this study did not at all lead to the

identification of the particular groups causing the effect, nor did it give the rôle of these levels in atomic structure (2 Chapters 13 and 14; 13 Chapter 8; 4, Chapter 12, 9).

The initial step in recognizing the stable groupings of the electrons and correlating them with chemical behavior by means of the periodic table of elements (see Table I) was due simultaneously to Gilbert Lewis and W. Kossel in 1917 (2; 5 Chapter 1, sect. 4; also 5 Chapter 9; 4 Chapter 11; and 13).

A glance at the periodic table (page 27) shows that there is one group of elements, designated as the eighth or 0 group of elements, which consists of gases that are chemically inert, i.e., that do not react chemically. These are the gases He, Ne, Ar, Kr, Xe, and Nt or Rn. It is also clear that these gases represent *a transition between two distinct types of chemical activity of the elements* immediately preceding them (univalent electronegative elements, F, Cl, etc.) and those which immediately follow them (univalent electropositive elements, Li, Na, etc.). This chemical inertness and the radically different behavior of the two neighbors, together with the idea of the variation of the nuclear charge by 1 unit as one progresses in the periodic table, led Lewis and Kossel to assign to the inert gas group the *stable electronic configurations*, an idea which had been so badly wanting.

To understand the situation a brief survey of the first period or two of the table is essential. Element 1 in the periodic table is hydrogen, nuclear charge $Z = 1$, with 1 electron. A hydrogen atom is electropositive and is chemically *reactive*, i.e., dynamically unstable. It reacts to do one of two things. It will either tie up to another hydrogen atom, giving a stable configuration, H_2 , with 2 nuclei $Z = 1$ each separated by a distance of some 10^{-8} cm, and 2 electrons which are now relatively stable, for molecular hydrogen is not very reactive. Or a hydrogen atom will even lose its electron to some atom like chlorine, forming a polar compound HCl in which the

TABLE I
PERIODIC CHART OF THE ATOMS
The Atoms Grouped According to the Number of Outer (Valence) Electrons

	-7 I	-6 II	-5 III	-4 IV	-3 V	-2 VI	-1 VII	0 VIII
H. 1.008	-7 +1	-6 +2	-5 +3	-4 +4	-3 +5	-2 +6	-1 +7	
Li. 6.940	3 9.02	4 Be	5 B	6 Al	13 10.82	14 12.000	15 14.008	16 N
Na. 22.997	11 24.32	Mg	26.97	28.06	31.027	32.064	33.457	35.91
K. 39.096	19 Ca	20	Sc	21	Ti	22	Cr	24
	40.07	45.10	48.1	50.96	52.01	54.93	Mn	25
29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr	
63.57	65.38	69.72	72.60	74.96	79.2	79.916	82.9	
Rb. 65.44	37 Sr	38 Y	39 Zr	40 Cb	41 Mo	42 96.0	43 96.2	44 Ru
	87.63	88.9	91	93.1	96.0	101.7	102.91	46 Pd
47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe	
107.880	112.41	114.8	118.70	121.77	127.5	126.932	136.2	
Cs. 132.81	Ba. 137.37	56	57-71 Rare *earths	72 Hf	73 Ta	74 W	75 Re	76 Os
	80 Hg	81	204.39	181.5	184.0	187.7	190.8	193.1
197.2	200.61	Tl	207.20	Pb	83 Bi	84 Po	85	86 Rn
87	Ra. 225.95	88 Ac	89	232.15	Pa. 90	U. 92	238.17	

57-71

Rare Earths

	I	II	III	IV	V	VI	VII	VIII
La. 138.90	57	58 Ce	59 Pr	60 Nd	61	Si 150.43	62 Eu	63
Gd. 157.26	64 Tb	65 162.52	66 Dy	67 Ho	68 Er	69 Tm	70 Yb 173.6	71 Lu 175.0

proton can ionize off in aqueous solution "preferring" its dynamical stability to electrical neutrality. A single electron is thus not a dynamically stable system. The second element is helium, nuclear charge $Z = 2$, with two electrons. This substance is quite *inactive* chemically. It requires more work to pull one electron out of helium than out of any other atom. It seems clear therefore that the helium structure represents one of the most stable configurations. Paired electrons such as in He are therefore a very stable configuration (possibly on account of the interaction of the fields produced by the electron spin). It should be noted that in H_2 the stability is produced by 2 electrons, and the stability of many if not most so-called *non-polar* chemical combinations can probably be attributed to the formation of stable cementing electron pairs (paired electrons of Gilbert Lewis). These are especially noticeable in the carbon compounds. Li with $Z = 3$ is the next element. It has 3 electrons, and since a pair of electrons would remain stable, the third electron may be expected to be unstable. It is characterized by an orbit of great ellipticity "keeping away" from the stable pair during the greater part of its motion about the nucleus. Li is one of the very electropositive elements which will shed its superfluous electron to any other configuration if possible. It even assumes the positively charged state in solution, yielding its electrical neutrality to gain the dynamical stability of the paired electronic grouping in helium without a third disturbing electron. Beryllium with $Z = 4$ and four electrons is apparently not able to gain stability with a group of 4 electrons, for two electrons apparently go to make a stable pair of the He type about the nucleus, leaving the other two electrons which do not pair up with great stability in rather elliptic orbits. This is manifested by the fact that Be loses two electrons quite easily, forming polar compounds which ionize as a divalent positive Be^{++} ion. Thus Be loses two electrons and its electrical neutrality to gain the dynamical stability of the

inert gas configuration, He, preceding it. The next element, boron, $Z = 5$, has a possibility of losing 3 external electrons to gain the dynamical stability of He. This it does, but with considerable reluctance, inasmuch as the energy changes involved in the loss of three electrons at once is such that in spite of the dynamical stability achieved the loss of electrical neutrality begins to be too serious a handicap. Beginning with B, the 2 electrons above the paired He group complete a second pair of electrons which continues as a constant but rather less stable group in heavier atoms. By this time the atom has "swelled" to such proportions that the next 2 electrons characteristic of C cannot form a stable group, and the stable grouping following is one of six electrons. Carbon, with $Z = 6$, can lose 4 electrons to gain the He configuration, but owing to the great loss of neutrality it in general reacts differently. It adds 4 more electrons in its combinations (e.g., with H in CH_4) forming stable groups of paired electrons which apparently can take on a very stable tetrahedral grouping about the inner 2 paired electrons of the He grouping close to the nucleus. Carbon may also in a sense share the 4 electrons with 4 atoms of an element like chlorine. Unlike the combinations of Li and Be with chlorine, this does not lead to polar molecules (15 p. 22), but the symmetry of the tetrahedral arrangement in CCl_4 makes a rather non-polar configuration. In cases where only 1, 2, or 3 of the 4 atoms about C are Cl the polar character of the molecule is evident.

Beginning with nitrogen, $Z = 7$, the 5 electrons outside the inner pair characteristic of He cannot form a paired group, but the number of outer electrons continues to augment until the number 6 is reached. These electrons therefore constitute part of a new stable grouping of 6 electrons which is only completed in neon. While N has 5 electrons all told, beyond the central He pair, and it can lose 5 electrons to an atom like O or Cl, forming pentavalent compounds of a complex sort, it can also

show in its more usual reactions a new tendency. The nearest inert gas to N is neon, $Z = 10$, with the inner pair of electrons typical of He, and a group of 8 outer electrons, containing the pseudo-stable external group of 2 characteristic of Be and another stable group of 6 more electrons characteristic of itself. These 8 electrons constitute the next really stable grouping after He, for Ne requires a great amount of work to detach one of these 8 electrons. By stealing 3 electrons, N can actually acquire a trivalent negative charge and also the electronic configuration of Ne. Thus it sacrifices its electrical neutrality to gain dynamical stability by becoming negatively charged. This leads to the formation of a polar compound, NH_3 or ammonia. NH_3 shows the characteristic behavior of a molecule which is not quite dynamically stable, for wherever it can it adds a fourth group, a proton H^+ , and forms the electrically charged but dynamically stable tetrahedrally symmetrical NH_4^+ ion. It might be said that the tetrahedral arrangement is a system of *molecular dynamic stability*, and not necessarily one of electronic stability about a nucleus.

Oxygen following N has a nuclear charge $Z = 8$, with the inner pair of electrons characteristic of He and 6 outer electrons. Here the tendency of losing electrons to atoms like chlorine of the seventh group is less pronounced than for N, though hexavalent oxygen compounds exist. It shows, on the other hand, a greater avidity for electrons, and by becoming negatively divalent it acquires the dynamical stability of neon and loses its neutrality. The O^- ion is therefore not uncommon in chemical reactions. The last element of this period, fluorine, has a nuclear charge of $Z = 9$, and just precedes Ne. While theoretically it could lose the 7 electrons external to the inner helium pair, it does not do so. It can readily pick up an electron from an atom like H or Na, forming a polar fluoride molecule which ionizes quite readily into F^- . Thus F loses its electrical neutrality, gaining a negative charge and the

stability of the Ne atom. Its activity is so great that it will even remove the 4 electrons of an element like Si, forming SiF_4 , which like CCl_4 because of molecular symmetry is non-polar.

After Ne comes sodium with $Z = 11$. Here we have first the paired He group, then the stable neon octette of 8 electrons, and finally an odd electron which revolves in an elliptic orbit characterizing the unpaired electron in Li. Like Li, Na readily loses its outer electron to gain stability. In an analogous manner, the increase of nuclear charges as we go down the table in a general way follows the procedure which we have already outlined. As, however, the value of Z increases, certain changes occur. While the increase in Z increases the force and reduces the size of the paired orbits of He on the inside because of the increased attractions, and of the 8 outer electrons and the later groups of electrons added, it is clear that eventually the atomic surface area to be filled by electrons increases and after the second octette of argon ($Z = 18$) has been added the new electrons take on groupings that are more complicated. This will be seen in the table of electron groupings shown in Table II, page 32.

A picture indicating the type of structure assumed for various types of atoms on the old Bohr theory is shown in Fig. 1. These pictures are now out of date, and the best formulation in terms of wave mechanics cannot give us such easily visualizable pictures.*

Before continuing to discuss the general table, one point may be added. It was stated that in early investigations two types of X-rays were distinguished whose spectra were quite constant and consistent, changing only their frequencies but retaining the same relative grouping of frequencies

* These pictures were drawn to illustrate a paper entitled Bohr's Atomteori by Kramers and Holst in 1923. At that time the designation of electron orbits did not conform to the correct designation as given in Table II. While the pictures are suggestive the wave mechanics has superseded them. A much more recent illustration by Kramers will be found in the International Critical Tables, Vol. I, page 47 (McGraw-Hill, New York, 1926).

TABLE II

Extra-nuclear Electronic Configurations

Element	Atomic number	Atomic mass	K 1 _s	L 2 _s 2 _p	M 3 _s 3 _p 3 _d	N 4 _s 4 _p 4 _d	O 5 _s
H	1	1.008	1				
He	2	4.00	1				
Li	3	6.94	1	1			
Be	4	9.1	2	2			
B	5	10.9	2	2 1			
C	6	12.0	2	2 2			
N	7	14.01	2	2 3			
O	8	16.0	2	2 4			
F	9	19.0	2	2 5			
Ne	10	20.2	2	2 6			
Na	11	23.0	2	2 6	1		
Mg	12	24.32	2	2 6	2		
Al	13	27.1	2	2 6	2 1		
Si	14	28.3	2	2 6	2 2		
P	15	31.04	2	2 6	2 3		
S	16	32.06	2	2 6	2 4		
Cl	17	35.46	2	2 6	2 5		
Ar	18	39.88	2	2 6	2 6		
K	19	39.1	2	2 6	2 6		1
Ca	20	40.07	2	2 6	2 6		2
Sc	21	44.1	2	2 6	2 6 1		2
Ti	22	48.1	2	2 6	2 6 2		2
V	23	51.06	2	2 6	2 6 3		2
Cr	24	52.0	2	2 6	2 6 5		1
Mn	25	54.93	2	2 6	2 6 5		2
Fe	26	55.84	2	2 6	2 6 6		2
Co	27	58.97	2	2 6	2 6 7		2
Ni	28	58.68	2	2 6	2 6 8		2
Cu	29	63.57	2	2 6	2 6 10	1	
Zn	30	65.37	2	2 6	2 6 10	2	
Ga	31	69.9	2	2 6	2 6 10	2 1	
Ge	32	72.5	2	2 6	2 6 10	2 2	
As	33	74.96	2	2 6	2 6 10	2 3	
Se	34	79.2	2	2 6	2 6 10	2 4	
Br	35	79.92	2	2 6	2 6 10	2 5	
Kr	36	82.92	2	2 6	2 6 10	2 6	
Rb	37	85.45	2	2 6	2 6 10	2 6	1
Sr	38	87.63	2	2 6	2 6 10	2 6	2
Y	39	89.0	2	2 6	2 6 10	2 6 1	2
Zr	40	90.6	2	2 6	2 6 10	2 6 2	2

TABLE II—Continued

Element	Atomic Number	Atomic Weight	Extra-nuclear Electronic Configurations					
			K 1 _s	L 2 _s 2 _p	M 3 _s 3 _p 3 _d	N 4 _s 4 _p 4 _d 4 _f	O 5 _s 5 _p 5 _d	P 6 _s
Cb	41	93.5	2	2 6	2 6 10	2 6 4	1	
Mo	42	96.0	2	2 6	2 6 10	2 6 5	1	
Ma	43		2	2 6	2 6 10	2 6 6	1	
Ru	44	101.7	2	2 6	2 6 10	2 6 7	1	
Rh	45	102.9	2	2 6	2 6 10	2 6 8	1	
Pd	46	106.7	2	2 6	2 6 10	2 6 10		
Ag	47	107.88	2	2 6	2 6 10	2 6 10	1	
Cd	48	112.40	2	2 6	2 6 10	2 6 10	2	
In	49	114.8	2	2 6	2 6 10	2 6 10	2 1	
Sn	50	118.7	2	2 6	2 6 10	2 6 10	2 2	
Sb	51	120.2	2	2 6	2 6 10	2 6 10	2 3	
Te	52	127.5	2	2 6	2 6 10	2 6 10	2 4	
I	53	126.92	2	2 6	2 6 10	2 6 10	2 5	
Xe	54	130.32	2	2 6	2 6 10	2 6 10	2 6	
Cs	55	132.81	2	2 6	2 6 10	2 6 10	2 6	1
Ba	56	137.37	2	2 6	2 6 10	2 6 10	2 6	2
La	57	139.0	2	2 6	2 6 10	2 6 10	2 6 1	2
Ce	58	140.25	2	2 6	2 6 10	2 6 10	2 6 1	2
Pr	59	140.6	2	2 6	2 6 10	2 6 10	2 6 1	2
Nd	60	144.3	2	2 6	2 6 10	2 6 10	2 6 1	2
Il	61		2	2 6	2 6 10	2 6 10 4	2 6 1	2
Sm	62	150.4	2	2 6	2 6 10	2 6 10 5	2 6 1	2
Eu	63	152.0	2	2 6	2 6 10	2 6 10 6	2 6 1	2
Gd	64	157.3	2	2 6	2 6 10	2 6 10 7	2 6 1	2
Tb	65	159.2	2	2 6	2 6 10	2 6 10 8	2 6 1	2
Dy	66	162.5	2	2 6	2 6 10	2 6 10 9	2 6 1	2
Ho	67	163.5	2	2 6	2 6 10	2 6 10 10	2 6 1	2
Er	68	167.4	2	2 6	2 6 10	2 6 10 11	2 6 1	2
Tm	69	168.5	2	2 6	2 6 10	2 6 10 12	2 6 1	2
Yb	70	173.5	2	2 6	2 6 10	2 6 10 13	2 6 1	2
Lu	71	175.0	2	2 6	2 6 10	2 6 10 14	2 6 1	2
Hf	72	178.0	2	2 6	2 6 10	2 6 10 14	2 6 2	2
Ta	73	181.5	2	2 6	2 6 10	2 6 10 14	2 6 3	2
W	74	184.0	2	2 6	2 6 10	2 6 10 14	2 6 4	2
Re	75		2	2 6	2 6 10	2 6 10 14	2 6 5	2
Re	75		2	2 6	2 6 10	2 6 10 14	2 6 6	1
Os	76	190.9	2	2 6	2 6 10	2 6 10 14	2 6 6	2
Os	76		2	2 6	2 6 10	2 6 10 14	2 6 7	1

TABLE II—Continued

Element	At. No.	Atomic Weight	Extra Nuclear Electronic Configuration												P		Q	
			K			L			M			N			O			7_s
				1_s	$2_s 2_p$	$3_s 3_p 3_d$		$1_s 2_p$	$3_p 3_d$		$1_s 2_p 3_d 4_f$		$2_s 2_p$	$3_p 3_d 5_f$		$1_s 2_p 3_d 4_f$		$2_s 2_p 3_d 6_s 6_p 6_d$
Ir	77	193.1	2	2 6	2 6 10			2 6	10 14		2 6	10 14		2 6	7		2	
Ir	77		2	2 6	2 6 10			2 6	10 14		2 6	10 14		2 6	8		1	
Pt	78	195.2	2	2 6	2 6 10			2 6	10 14		2 6	10 14		2 6	8		2	
Pt	78		2	2 6	2 6 10			2 6	10 14		2 6	10 14		2 6	9		1	
Pt	78		2	2 6	2 6 10			2 6	10 14		2 6	10 14		2 6	10			
Au	79	197.2	2	2 6	2 6 10			2 6	10 14		2 6	10 14		2 6	10		1	
Hg	80	200.6	2	2 6	2 6 10			2 6	10 14		2 6	10 14		2 6	10		2	
Tl	81	204.0	2	2 6	2 6 10			2 6	10 14		2 6	10 14		2 6	10		2 1	
Pb	82	207.2	2	2 6	2 6 10			2 6	10 14		2 6	10 14		2 6	10		2 2	
Bi	83	208.0	2	2 6	2 6 10			2 6	10 14		2 6	10 14		2 6	10		2 3	
Po	84	210.0	2	2 6	2 6 10			2 6	10 14		2 6	10 14		2 6	10		2 4	
Eka I.	85		2	2 6	2 6 10			2 6	10 14		2 6	10 14		2 6	10			
Rn	86	222.0	2	2 6	2 6 10			2 6	10 14		2 6	10 14		2 6	10		2 5	
Eka-C's.	87		2	2 6	2 6 10			2 6	10 14		2 6	10 14		2 6	10		2 6	
Ra	88	226.0	2	2 6	2 6 10			2 6	10 14		2 6	10 14		2 6	10		1 2	
Ac	89	227.0	2	2 6	2 6 10			2 6	10 14		2 6	10 14		2 6	10		2 6 1 2	
Th	90	232.15	2	2 6	2 6 10			2 6	10 14		2 6	10 14		2 6	10 1		2 6 1 2	
Th	90		2	2 6	2 6 10			2 6	10 14		2 6	10 14		2 6	10			
Pa	91	230.0	2	2 6	2 6 10			2 6	10 14		2 6	10 14		2 6	10 2		2 6 2 1	
Pa	91		2	2 6	2 6 10			2 6	10 14		2 6	10 14		2 6	10			
U	92	238.2	2	2 6	2 6 10			2 6	10 14		2 6	10 14		2 6	10 3		2 6 3 2	
U	92		2	2 6	2 6 10			2 6	10 14		2 6	10 14		2 6	10		2 6 4 2	

throughout (2 Chap. 13). These were the *K* and *L* series of X-rays distinguished by C. G. Barkla. With the discovery of the crystal method of X-ray analysis, the frequency relations of these lines were recognized, and it was Moseley who ascribed the change in frequency to a *change in nuclear charge Z* which did not affect the configuration of the electrons. As a result of Moseley's work it was soon recognized that the *K* series X-ray lines really began with He and were the spectra produced when the inner group of paired electrons in the atoms were disturbed. These *K* lines continue right up to the heaviest element known, UrI, $Z = 92$, and are in this element the shortest wavelength X-rays known to be due to the extranuclear structure. Hence we know that the inner electronic level is the paired electron group of He which gives the *K* series of X-rays and varies

in frequency by virtue of the change in Z only. This inner group, shell, or level of electrons is called the K X-ray group, shell, or level, and will henceforth be so designated. In an analogous manner the L series of X-ray frequencies have been ascribed to the first complete octette characteristic of Ne when it is disturbed. Its frequencies vary only with the effective nuclear charge acting on them, that is Z minus 2, for the 2 K electrons are inside. This series begins with Ne and goes right on through the set of elements up to UrI. The frequencies are obviously lower than those of the K level. With the completion of the next inner level with scandium, still another group of X-ray spectra are recognized, and these are called the M level lines, corresponding to the M level or shell of electrons. In a similar way, as each new shell of electrons is added and structurally completed, successively, the N , O , P and Q levels of X-rays appear. Thus, while C has essentially only the K series X-rays, UrI has the K , L , M , N and O levels complete with P and Q levels filling.

Table II, pages 32–34, gives the following data: First, the symbol of the element; next, Z , its nuclear charge or atomic number; and third, its atomic weight. The succeeding 7 columns, labeled K , L , M , N , O , P , Q , give the electron shells or stable electron groupings as they occur in the atom, the L shell being on the average outside the K , the M outside the L , the N outside the M , and so on (2 Table 5 appendix). In each of these are given a series of sub-groups labeled 1_s for the K level; 2_s and 2_p for the L level; 3_s , 3_p and 3_d for the M level; 4_s , 4_p , 4_d and 4_f for the N level, and so on. The 1_s group contains the stable helium doublet or pair characteristic of the K series. The 2_s group designates the second pair of electrons outside the K level, beginning with Be which forms a pseudo-stable subgroup in the L shell. The 2_p group constitutes the 6-electron group in the K level, which is completed with neon. The 3_s is the next pseudo-stable grouping of 2 about the Ne octette which appears with Mg; the 3_p is the group of 6 in the M

level which completes the stable group of 8 characterizing argon.

With further increase in atomic number, the electrons do not complete the M level by filling in the 3_d grouping. Instead, two electrons go into the 4_s level completing the 4_s shell as seen in Ca. Thereafter the 3_d shell begins to fill up as Z increases, being complete with 10 electrons in Cu which has stolen one 4_s electron to complete the 3_d shell. From then on the 4_s shell is completed in Zn, and the 4_p shell begins to fill up to 6 in Kr, the next inert gas. It is seen that Kr has *the same outer electronic shell* as Ar, but in acquiring it (due to the increase in surface of the atom) gained 18 electrons. This constitutes the first long period, characterized by 18 electrons.

In the second long period, from krypton to xenon, a similar process of adding on electrons as Z increases is seen to take place. Following Kr, the next two electrons go into a 5_s group of 2 before the 4_d group and 4_f group are

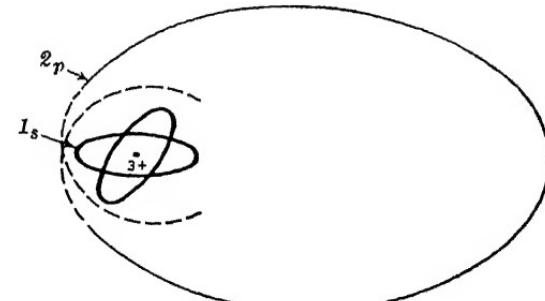


FIG. 1c.—The Atomic Structure of Lithium.



FIG. 1b.—The Atomic Structure of Helium.

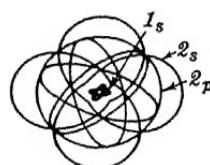


FIG. 1d.—The Atomic Structure of Neon.

filled in the element Sr. As soon as the 4_d and 5_p groups are filled we reach Xe, an inert gas, with atomic number 18 units greater than Kr and 18 more electrons. From then

on the process of filling the shells becomes still more complex, for now the 6_s group in Ba is filled while the 4_r , 5_d , and 5_f groups must be filled. To do this requires 32 electrons.

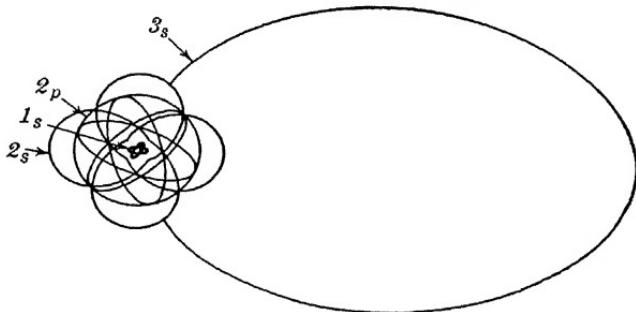


FIG. 1e.—The Atomic Structure of Sodium.

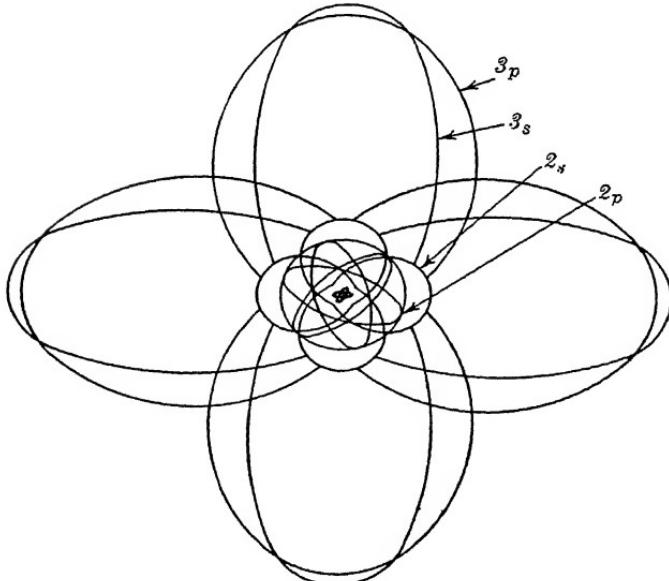


FIG. 1f.—The Atomic Structure of Argon.

trons which also go to fill the 6 places required in the 6_p shell of the P level and give the inert gas niton, or radon, whose nucleus is radioactively unstable. It is seen that in

this complex process of filling the shells the outer group of electrons is little changed, and the essential chemical characteristics of the elements vary very little. The elements are more or less metallic, as the two outer electrons are more or less easily removed. Furthermore, the small change in the outer configurations results in the relatively feeble chemical differences characterizing the rare earth elements. In fact, the last element to be found in this group could be detected in a mixture only by its X-ray spectrum, as it could not be separated chemically in pure form. Beyond Rn (or radon) few elements further exist, as the heavy nuclei of atomic number above 82 are unstable and undergo radioactive disintegration.

We can, therefore, say that in the atom there are certain fundamentally stable dynamical configurations of the electrons which lead to the inert chemical group of gases, the eighth group in the periodic table. These stable configurations consist of: the helium pair, then followed by the neon octette, surrounded in turn by the argon octette, surrounded in turn by the krypton group of 18 which is characterized outside by an octette, surrounded in turn by the xenon group of 18 having as its outer member an octette, and finally surrounded by the radon shell of 32 electrons with the outermost unit the octette. We thus see that chemical or dynamical electron stability is characterized fundamentally by 2 groupings, the helium paired electrons and an octette consisting of a subgroup of 2 electrons and one of 6 electrons. In more complex atoms of high Z , before the octette can complete itself, the intervening groups must be completed, giving octettes or stable groups at intervals of 18, 18, and 32 electrons, respectively, in the long periods. Possibly the shortest way of summarizing the stable electronic configurations in atoms of increasing Z is to say that the stable groups or levels have 2, 8, 8, 18, 18, and 32 electrons.

We may summarize this whole section on the extra-nuclear structure by saying that for each value of the

nuclear charge Z the Z electrons must be added to surround the nucleus in some unknown fashion. For convenience we ascribe to the electrons complex orbital motions governed by quantum laws. These, together with numerous data of chemical and spectroscopic nature, allow us to make conclusions as to the way in which the electrons are grouped in atoms for which Z is specified. The electrons group or associate themselves in a number of stable configurations about the nucleus which remain practically inviolate units on the further addition of electrons for atoms of higher Z . The shells, or groups, can be definitely located by the energy required to cause the electrons to be disturbed or removed from the atom, and from the energy relations we can locate the groups in various levels of the atom corresponding to the energy of binding of the members of the group. These levels are characterized by the type of X-ray which they emit when disturbed, such as the K , L , M , N , O , and P electron shells or levels, the innermost shell being the K shell, or level. The numbers of electrons associated with each shell or level arrange themselves in stable groups which are represented in the periodic table by the inert gases. The numbers of electrons in each of the stable groups are known, and the structure of such atoms is clearly designated into levels and subgroups by an appropriate table. The stable groupings of electrons in the inert gases are as follows:

He 2, Ne 8, Ar 8, Kr 18, Xe 18, Rn 32
and they consist of

	K	L	M	$M-N$	$N-O$	$N-O-P$
He.....	2					
Ne.....	2	8				
Ar.....	2	8	8			
Kr.....	2	8	8	10-8		
Xe.....	2	8	8	10-8	10-8	
Rn.....	2	8	8	10-8	10-8	14-10-8

The chemical behavior and in general all the physical behavior of the atoms which is not due to mass alone must be correlated with the outer electronic configuration, for it is these electrons only which determine the relation of an atom to its neighbor, and in general physical processes, except those involving high energies, it is only the outer electrons that are affected by changes. As regards the chemical behavior of the atoms, we can summarize the situation quite simply by saying that this is governed by the tendency of the outer electrons of the atoms to reach dynamical stability by joining forces with electrons in similar or different atoms to achieve stable electronic configurations about or between the two or more atoms involved, as the case may be. Since the chemically and dynamically stable configurations of the electrons are those evidenced by the inert gases He, Ne, Ar, etc., characterized by the paired electron group or the octette, we can say that in general two atoms will react if they do not have all their electrons in paired groups or in octettes, when they can arrange their outer electrons in one or the other of such groups by combining or reacting chemically.

An *electropositive* element is one which gains the dynamical stability of a pair or an octette by *losing* its outer electrons to some other element. An *electronegative* element is one which gains the dynamical stability of a pair or an octette by *adding* extra electrons to its outer shell thereby becoming negatively charged. In general, combinations of such a type between electropositive and electronegative elements result in a displacement of the electrical centers in the molecule so formed as to give an electrical dipole, or electrical moment (15 Chapters 3 and 4). Such molecules are called polar, and in solutions of high dielectric constant they in general dissociate to give charged atoms or molecular radicals, the electrolytic ions. Thus the atoms lose their electrical neutrality to gain dynamical stability. Polar compounds are largely bound together by their electrostatic forces.

In other cases, such as in molecules of H_2 , N_2 , or O_2 , and compounds of carbon, the dynamical stability is reached through the pairing of the otherwise unstable outer-shell electrons with electrons of other like or unlike atoms. Such non-polar compounds thus depend largely on paired electrons for their stability. These fundamental tendencies are also supplemented and strengthened by the possibility of the formation of stable groupings of the *atoms relative to each other*. A stable grouping where the establishment of electron pairs leads to a symmetrical tetrahedron of atomic centers is such a modifying factor. It leads to the formation of the endless organic combinations of carbon, or the formation of ions, such as the NH_4^+ ion. Other tendencies are doubtless present, but they have not been clearly recognized.

It is thus seen that recognizing a few fundamental tendencies and knowing the stable electronic configurations, we can at once more or less accurately foretell what in general the characteristics of an element of given atomic number will be, and how it will react with another element of given atomic number.

6. Molecular Structure.—It is next necessary to discuss briefly a few points concerning molecular structure (15 chapters 3 and 4) before going on to the kinetic nature of a gas.

With the general picture of the nature of atoms and the rules determining the way in which they combine (formation of octettes, or stable electron pairs, and spatial arrangements appropriate to the forces and units involved), it is not difficult further to describe the structure of the molecules. To do this it is best to pick a few typical examples at random to clarify the subject.

In the case of the hydrogen molecule, the two protons form two mass points separated by about 0.75×10^{-8} cm.* About this system of two protons the two electrons in

* When excited, the distance between the nuclei can in this case increase to about 1.2×10^{-8} cm⁸.

the normal atom move in some sort of orbits or configuration the dimensions of which it is impossible to estimate. The old kinetic theory gives a molecular diameter of 2.3×10^{-8} cm in the normal unexcited state. The instantaneous positions of the electrons must normally be between these two distances, namely, 0.75×10^{-8} and 2.3×10^{-8} cm. The two mass points can revolve about two axes at right angles to each other and to the line joining the points. This gives the well-known rotation of the hydrogen molecule which is the cause of the appearance of the many-lined spectrum (in other molecules the *band* spectrum) observed for molecular hydrogen. The rotary motion of the two nuclei, as in fact all periodic atomic motion, is quantized, that is, the moment of momentum of molecular *rotation* is some whole multiple of $h/2\pi$. The frequencies of rotation have thus discrete values and are not continuously distributed through a large range of values. As the molecule rotates slowly compared to the electronic frequency, due to the well-known Doppler principle, light waves emitted by disturbed electrons will appear lengthened or shortened in wavelength as the motion of the electron in the molecule in the line of sight is one of advance or recession. Hence for *each value* of the moment of momentum *two lines* will appear, one on each side of the normal line emitted by the excited molecule which does not rotate.

The centripetal forces of such a rotating molecule will of course cause a *slight increase* in the distance between the two nuclei, and of the diameter of the electron orbit as well, i.e., rotation causes a slight "swelling" of the molecule. Again if one or both of the electrons in the molecules are disturbed by some external agent, either light or impact of a rapidly moving particle which gives them an energy E corresponding to the transition to a higher state, it is clear that the binding forces should be altered. The distance between the nuclei will increase, and in some cases the molecule will become unstable. If the energy given an electron is greater than the work needed to separate the atoms, i.e.,

in case one electron is removed from the molecule, dissociation may follow. In H_2 it was believed that this could not take place of itself, though in some molecules it appears to be the case. In H_2 an impact with another molecule was supposed to be needed, once the molecule is disturbed to a sufficiently great degree, before the pair will separate, but recent results render this doubtful (R 61). In case one electron was removed, the molecule after collision separates into a charged atom and a neutral one. If the removal of one electron to an outer orbit only takes place, the electron generally remains in the outer orbit but a short time, 10^{-8} seconds. It then returns under the emission of light. If the disturbance was such as to make dissociation of the molecules into atoms possible, the needed dissociating impact with a neutral molecule must occur within the 10^{-8} seconds before the electron sinks to its former level.

In addition to rotation the two nuclei can vibrate towards and from each other along the line of junction. In general this vibration requires a large amount of energy compared to rotational energy. It is, on the other hand, less than the energy required to cause an electron to move to an outer orbit. Hydrogen in the unexcited state at room temperature does not receive enough energy to cause a vibration, while it shows rotation. If the temperature goes well above $1000^\circ C.$ vibrations are set up on account of the violence of impacts with other molecules. By cooling hydrogen down to liquid air temperatures the impacts become so feeble that not even enough energy is given to initiate a quantum of rotation; hydrogen at this temperature shows no rotation and the spectrum is simplified. The molecule acts as a single mass point. Above $1500^\circ C.$ the impacts are so violent that the amplitude of vibration occasionally reaches magnitudes such that the molecules dissociates into two atoms. Since the energy changes involved in electron transitions are greater than in vibrational changes, it is clear that electron jumps in an atom will also cause the initiation of vibrational motion. Hencee

INTRODUCTION

even at low temperatures when molecules have electrons disturbed by bombardment with free electrons, as in a glow discharge tube, vibrational effects are observed. As in the case of rotations, so in the case of vibrations, the Doppler effect causes shifts of wavelength depending on whether the motion of the nuclei in the line of sight is towards or away from the observer, for many light waves are emitted during one vibration.

Since the energies are greater in vibration and since the vibrations are quantized just as are rotations, a series of frequencies will appear for the various quanta of vibration. These series of vibrational levels are separated by considerably larger distances than the rotational levels. Obviously the vibrations will alter the binding forces and hence the apparent size of the molecule. The spectrum of a molecule excited to three successive electron orbits will thus show an appearance as indicated in Fig. 2. A more complete discussion of the picture of a spectrum can be found in 2 Chapter 9; 4 Chapters 9 and 10; 5 Chapters 7, 10, 12, and 18. The longer lines, A_1 , A_2 and A_3 , correspond to excited electron levels. The secondary lines, B_{1-2} , B_{2-2} and B_{2-1} , drawn shorter to distinguish them, represent vibrational levels set up in each electronic level. The very short lines, labeled C_{A_1-1} , $C_{A_2, B_{2-1}-2}$, and C_{A_3-2} , which experimentally in a spectrograph would appear just as long as the others, represent the rotational levels. The groups of lines B_{1-2} , B_{2-2} and B_{2-1} represent separate bands, while the whole represents a band system. This idealized sketch is much complicated in reality by overlapping, absence of lines, and certain details of fine structure. Such details of fine structure, for example in hydrogen, are ascribed to the minute effects in the nucleus due to the alignment of the supposed magnetic moments of the protons because of proton spin. This spin causes two different magnetic configurations of the protons in the H_2 molecule, leading to the so-called ortho and para hydrogen recently discovered, through minute differences in the fine

structure of the lines, by Bonnhofer, and also observed in specific heats. Other irregularities are due to perturbations of particular orbits by possible other orbits of equal energy differences (R 9).

As regards the external effect of all these elements, namely, rotation, vibration, and electronic excitation on the molecule, the changes are relatively unimportant until dissociation takes place. The kinetic theory, as we shall see, assigns an external diameter to the hydrogen molecule which is the effective diameter of a hard elastic sphere which in collision and interactions with like molecules would produce the same effect on the gaseous behavior as the true hydrogen molecule. Actually the molecule is probably not even nearly spherical in shape, nor is it in any sense a hard elastic sphere. It consists of a system of two protons with two electrons performing rapid motions in some kinds of orbits about them. These are surrounded by electric and magnetic fields of force (the electrical forces predominating) such that when two molecules approach each other at a given speed they are enabled to approach to a certain distance before the mutual distortion of the electric fields gives restoring forces that cause the motion of approach to cease and the motion to reverse in sign. It is probable that even with the same

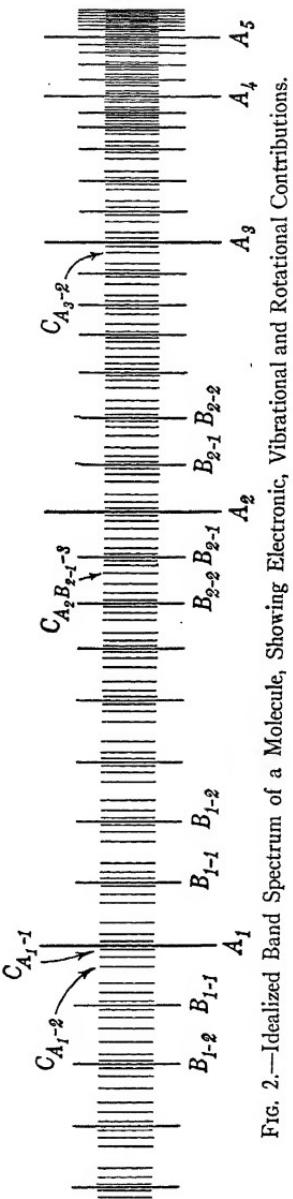


FIG. 2.—Idealized Band Spectrum of a Molecule, Showing Electronic, Vibrational and Rotational Contributions.

speed two H₂ molecules approaching with the protons of each lying on parallel lines perpendicular to the motion would have a collision in which the distance between centers of gravity of the two molecules at closest approach would be very different from the case where the four protons lay along the line of motion. The changes in diameter produced by rotation and vibration, together with the differences due to orientation in impact, will, in general, be beyond detection in the crude statistical analyses of molecular diameter which are possible in experiments from the kinetic theory point of view. Such an analysis, as will be seen, leads us to rough approximations only, which, however, suffice for calculations in the fields of gaseous discharge where experiments are indeed still crude, owing to the complexity of the phenomena.

In addition to the repulsive forces on close approach, produced by the repulsive fields of the external electrons of two molecules, another set of forces comes into play, namely, those of attraction (10 p. 159 ff; 21 Chapters 1 and 2). This may seem paradoxical at first but is not in reality so. Molecules and atoms are complex dynamic configurations of electrons and protons or positive nuclei in space. Such a spatial distribution of positive and negative charges, even though as a whole equal in number, is in reality surrounded by a complex field of force. To visualize this all one need do is to regard a bar magnet with two equal and opposite poles when placed under a piece of paper, with iron filings shaken over it. Even at greater distances such a dipole, distant r cm from a single pole of unit strength, will act on that pole with a force:

$$f = aml/r^3 \quad (18)$$

where a is a numerical factor depending on the orientation of the axis of the bar magnet, m is the pole strength of the bar magnet, l the distance between the poles, and r is the distance of the unit pole from the bar magnet. Hence it is not surprising that two such bar magnets at a distance r

should attract each other if oriented in the proper manner. The field of force produced at some distance by two such dipoles, that is, 2 electrons and 2 protons (the electrons lying at alternate corners of a square) again produces a field of force which varies as the inverse fourth power of the distance, while an octopole produces a field varying as the inverse fifth power of the distance. Such fields act to produce distortions of neighboring molecules in such a way as to bring further moments into play, and such distortions are always attractive. Thus the simple case of a single + charge acting on a neutral molecule produces an electron displacement in the molecule giving a dipole. The dipole strength, that is, el , depends on the + charge and on $1/r^2$, where r is the distance between molecule and charge. But the dipole attracts the charge according to an e^2l/r^3 law in analogy to the case of a bar magnet and an isolated pole. Hence, the force between a neutral molecule and a plus or a minus charge at a considerable distance is expressed by:

$$f = a e^2l/r^5 \quad (19)$$

This law will be encountered frequently in the study of gaseous ions, and doubtless is of importance in all dielectrics.

If, however, the molecules come very close together, e.g., so that the distances between the outer electron shells of the two molecules are of the order of magnitude of the diameter of the molecules, the case is altered. There is a limit to the distortion of the electronic shell or orbit system in a molecule. The outer electronic systems closely approaching each other are mutually repelled more strongly than the compensating attractions of the nuclei can account for (the electron shells approach to within very small distances of each other while the average distances of the electrons and nuclei are not radically changed). Thus repulsive forces of a very high order of magnitude come into play. In fact the repulsive forces between the electron shells of atoms on close approach vary as $1/r^n$, where n

INTRODUCTION

can have values from 7 to 11 or more. Hence we can nicely represent the molecular force fields by a diagram. Plotting attractive forces upwards above the axis of abscissae and repulsive forces downwards below the axis, since they are negative, we get the diagram of Fig. 3.

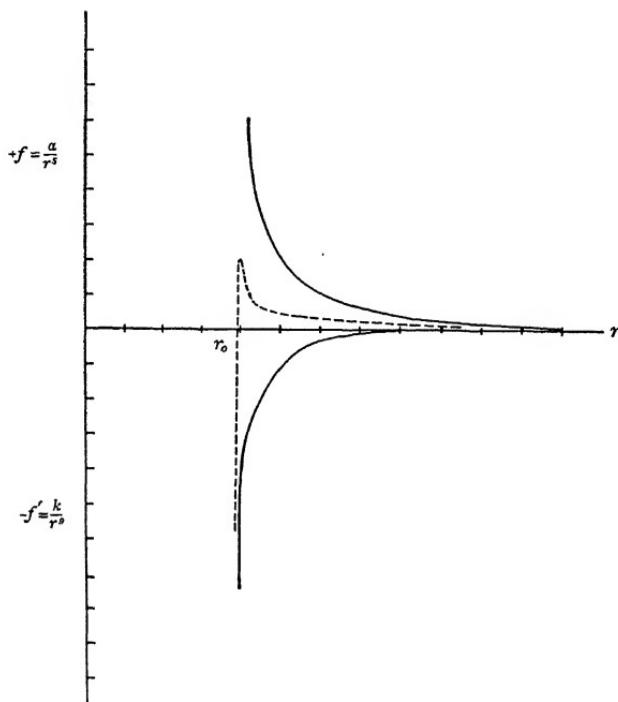


FIG. 3.—Molecular Force Fields, Illustrating the Effect of Simultaneous Action of Attractive and Repulsive Forces.

The resultant force at any r is given at once by the dotted line which is the difference $f - f'$. As seen it rises to a maximum and plunges sharply downward, crossing the axis at r_0 , then becoming negative, i.e., repulsive. The point r_0 is the point at which two molecules with no velocities will approach each other away from all other mole-

cules. If the molecules move relatively to each other, they will approach to a value of r less than r_0 , which is the smaller the faster the molecules are moving, and hence the closer they can approach each other before the velocities are annihilated by the repulsive forces. At distances below r_0 the resultant force increases rapidly with decreasing distance; therefore, the mean distance of approach decreases but little as velocity increases, but it does decrease. It might be possible to call r_0 the average distance of approach and call half this distance the radius of a single molecule. Since the forces are not symmetrical about a molecule, it is clear that r_0 will depend somewhat on the orientation of the two molecules. For simplicity in mathematical treatment, molecules are theoretically treated as spheres. This is, however, an *artifice* for mathematical simplicity only (10 p. 160 ff).

For hydrogen-like molecules the forces of attraction are relatively feeble, making the constant a in Eq. 19 rather small. We must go down to low temperatures, i.e., small velocities of molecules, before the attractive forces can have values of the potential energy equal to the kinetic energy of agitation. At the point where this equality is approached the slower molecules "capture" each other, i.e., execute closed orbits about each other, and *condense* to the liquid state. In fact, hydrogen has one of the lowest boiling-points of the molecules known. Helium, a monoatomic gas, has the lowest value of a in the force equation (Eq. 19) and is the lowest-boiling liquid known.

The values of the variation of f with r are not calculable directly. However, from the variation of viscosity with temperature, from the boiling-points, and from such factors as compressibilities, we can estimate the actual variation of f and f' with r . This leads to the values of $f \propto (1/r^5)^*$ and $f' \propto (1/r^n)$ where n varies from 7 to 11.

Next to molecules like H_2 , we can consider, as similar in general behavior, molecules like N_2 , O_2 and CO , in

* \propto means "varies as."

which the binding is due either to paired electrons or the formation of an outer electronic grouping of an octette with no serious dissymmetry. O_2 is doubtless based on a pairing of electrons, while N_2 and CO are arranged so as to have an outer electronic octette. N_2 is very much like argon in its general behavior. All these gases have very small values of a in the attractive forces, so that they have low boiling-points. Their stability is attested by the fact that the atoms do not separate easily and are strongly bound together (their energy of dissociation is from 6 to 11 volts). In this respect other homopolar or non-polar molecules, like the halogens Cl_2 , Br_2 , and I_2 , differ in being much less closely bound, and in fact all these latter molecules dissociate quite readily, especially under the influence of radiation (their dissociation energy is less than 2 volts). These molecules are also bound together by binding perhaps analogous to that in N_2 and O_2 . However, the numbers of electrons which the halogen atoms possess in their outer shells, 7 each, do not lead to stable electronic configurations as well as the 6 electrons of oxygen or 5 electrons of nitrogen, or 4 and 6 electrons of C and O in CO.

In molecules like CH_4 and other carbon compounds, we have the pairing of 4 electrons of carbon and the electrons of H together with the arrangement of the 4 protons of H with their electron pairs at the corners of a regular tetrahedron.

The other class of compounds are those formed between atoms of widely different electron affinity, for example, H, Na or Li and Cl, Br, I or O. In such compounds the electron from the more positive element is *transferred* to the more negative element. In such configurations the electrical constituents of the molecule are separated in the molecule giving a *permanent* electrical moment or dipole (15 Chapters 3 and 4). Such molecules are called polar molecules, and are at once recognized by their separation in aqueous solution to ions, though this is not always the case. In HCl (which is a typical strongly polar compound)

the one electron of the H atom goes to make the octette of the Cl atom with the 7 valence electrons of Cl. The proton, while not completely outside the shell of 8 of this octette, lies relatively far from the Cl nucleus with its *K* and *L* shells of electrons complete. However, the separation of the center of negative electrification about the Cl nucleus and the proton leads to an electrical moment which acts as if there were in HCl a single proton and a single electron separated by 0.2×10^{-8} cm. or about 0.14 of the diameter of the molecule, while the H and Cl nuclei are 1.276×10^{-8} cm apart. In NaCl the Na nucleus is inside but may well be quite near the surface of the electronic octette due to the valence electron of Na and the 7 electrons of Cl. When the NaCl molecules are cooled to a temperature where they settle down into a solid geometrical arrangement in the rock salt crystal, the Na⁺ and Cl⁻ ions are *quite separate*, and we have a crystal composed of a space lattice of Na⁺ and Cl⁻ ions in a cubical lattice with Na⁺ ions and Cl⁻ ions alternating at the corners, so that each Na⁺ ion is surrounded by 6 Cl⁻ ions, and vice versa. When placed in aqueous solution the crystal dissolves probably as separate ions of Na⁺ and Cl⁻. The electrical moments of such molecules are so pronounced that they manifest their presence by giving high dielectric constants in the gaseous state which have a marked temperature variation, indicating the presence of molecular dipole moments of a permanent sort. Such conditions hold as well for all salts of the types of CaCl₂, AlCl₃, etc.

Another important group of polar compounds arises from the union of atoms of hydrogen with oxygen, either alone or in combination with other atoms. The simplest case is that of water. Here two H atoms give up electrons to an O atom to complete the octette of the O atom. For some reason, not yet clear but possibly associated with proton spin, the formula for H₂O is not the symmetrical arrangement of HOH previously assumed for water, with the two protons inside but near the surface of the

outer octette of oxygen, and lying along a single line. Such a configuration, having oppositely placed proton-oxygen dipoles, has no electrical moment, while water has one of the strongest electrical moments of any molecular dipole known. The two protons probably lie inside the outer-oxygen octette, but in such a way that they form a triangle, with the oxygen nucleus as the vertex, having an angle of closely 64° . Thus H_2O has the form of a triangle with an angle of 64° at the vertex * and possessing a powerful electrical moment (15 Chapter 4). These dipoles in the liquid state presumably arrange themselves in associated groups, giving still greater electrical moments and giving us a liquid with a dielectric constant of 81. The replacement of one of the protons by a CH_3 group, or by a carbon atom with a long carbon chain attached, still does not destroy the moment of the water grouping, and all the alcohols are characterized by strong dipole moments. The same is true of the alkali metals which replace one of the hydrogens of HOH, giving the hydroxides. In these compounds the more metallic and bulky alkali ions Na^+ , K^+ , etc., dissociate off more readily than the proton of water, and we have the alkaline behavior. In other combinations of carbon and oxygen, the carbon attaches two oxygen atoms, one of which has a hydrogen atom attached in the well-known $\text{C}_{\text{O}}^{\text{OH}}$ group characterizing the organic acids. Here the proton appears to dissociate off the more readily.

Another group of polar molecules are those formed of carbon combined with one or more hydrogens and a halogen or two. Here again the electron of the carbon (which in CH_4 would have paired with an electron from one of the H atoms) now goes to the Cl, and in such a compound as CH_3Cl we have again weak but recognizable electrical

* Two models are possible with angles between the lines joining the protons to the O nucleus, 64° and 110° . From the values of the electrical moments observed, the former seems the most probable.

moments. When we replace all the 4 hydrogen atoms by Cl, as in CCl_4 , the tetrahedral symmetry of the CCl_4 molecule annihilates the electrical moments, and we have a practically non-polar compound. Combinations of nitrogen and oxygen together with carbon compounds form strongly polar molecules such as nitrobenzol, $\text{C}_6\text{H}_5\text{NO}_2$. In the case of the unsymmetrical ammonia, where the 3 electrons of 3 H atoms go to an octette about the nitrogen with the protons just inside the octette, there is still a permanent electrical moment. When a fourth proton joins the group to make the NH_4^+ ion, the complex, while charged, probably has no moment, though when this unites with a Cl^- ion to make NH_4Cl the electrical separation forms a very polar compound analogous to NaCl.

Perhaps one more point regarding molecule formation might be brought out. While in general in the gaseous state the inert gases are monatomic as are the vapors of many metals, such as Na, K, Hg, and Cs, there are cases where this is no longer true. In cooling these metal vapors down near their condensation temperature, the atoms begin to join together, at first as diatomic molecules and later in larger aggregates. The presence of such molecules is shown by the presence of band spectra in emission and absorption for these vapors. Again, even He atoms will unite to form He molecules. Such chemical reactions of the inert gases generally occur only under conditions of electrical excitation, and the existence of molecules of He is a very transitory phenomenon. We might in fact regard the formation of He_2 as the result of a disturbance of the normal atomic He doublet by the raising of one of the electrons to a higher energy level. In fact, a different set of orbits or states due to excitation is also observed in atomic He as the so-called metastable state. In this condition the He atoms, though having a high potential energy, can remain for periods 10^4 times or more of the time spent in the normal excited state of 10^{-8} secs.

This brief survey of molecular constitution leads us to

see that by means of pairing of electrons and octette formation we may obtain stable dynamical configurations which, depending on the nature of the atoms, may have complete electrical symmetry or incomplete electrical symmetry of all degrees. This leads to non-polar molecules or polar molecules with high electrical dipole moments. The forces between molecules are in general similar to those between hydrogen molecules, and the non-polar compounds with stable outer electronic configurations have in general weak attractive forces of the a/r^5 type. For the polar compounds a may be very large, and in general such compounds are solids or liquids at ordinary temperatures, while the homopolar compounds are more or less permanent gases. The importance of these differences in types of molecules will become evident when we come to a study of gaseous ions.

Recognizing the fact that the attractive forces of the molecules (even in such cases as H_2) exist and can play a considerable rôle well beyond the confines of the molecule, we shall not be surprised to see these cohesive forces manifesting themselves in other ways. If a surface of glass or metal is exposed to a gas, the gas molecules bombarding the surface may at times exert such forces on the surfaces of the metal that the gas molecules combine with the surface atoms. For at the surface of a solid the atoms and molecules have electrical fields that are not as completely saturated as they are inside the surface. It thus happens that most gas molecules will "condense" on the surfaces of solids in mono-molecular layers and at higher gas pressures and lower temperatures in even thicker films. In some cases the forces and energy relations of the gas molecules and surface atoms or molecules may be such that the atoms form secondary chemical combinations with the molecules (10 Section 84). Thus oxygen, hydrogen, and CO will form a layer of gas on platinum which does not evaporate off as the temperature is increased. They can only be removed by admitting a gas which reacts with them

chemically at the surface. Thus a layer of CO will adhere to Pt until oxygen is admitted to remove the CO by forming CO_2 , and replace the CO by oxygen from the super-abundance present. It is possible that such combinations of Pt and adsorbed gas may result in the dissociation of the molecules, forming loosely bound reactive atoms. Such surfaces are called catalytic surfaces.

In other cases, the molecules not only adhere to the surface but actually dissolve in the metal, as is the case with H_2 in palladium and with H_2O in glass. These adsorbed substances are very difficult to remove, and such adsorbed surface layers and adsorbed substances probably play important roles in the behavior of dielectrics and in their breakdown. They certainly play a rôle in sparking phenomena in gases, as they change the emissive properties of electrodes for electrons and hence alter sparking conditions. Thus the denuding of a metal surface of its gas film decreases the electron emission in some cases and leads to very high values of the sparking potential, while oxide films may also decrease electron emission and increase the sparking potential difference.

We have now gained a fair general idea of the nature of the complex electronic structures which constitute the outer portions of atoms combined together in the form of molecules. We have seen that the nuclei are in general inside the outer electronic structure, but not always symmetrically placed with respect to the electrical center of the system. This fact is evidenced at once by the presence of molecular dipoles. In other structures the configurations are quite symmetrical and no permanent dipoles are detectable. The distances between the nuclei and their masses lead to the existence of molecular moments of inertia. The mass points can therefore undergo rotation about a common center of gravity. They can further vibrate along the lines of junction. Changes in the electronic orbits, as well as rotation and vibration, lead to changes in the distance between nuclei and hence to changes in the

sizes of the molecules. The sizes of the molecules as physically studied by kinetic theory methods depend on the average distance of approach of molecular centers in impact. These are governed (*a*) by the energies of the molecules in impact, (*b*) by the directions of approach, and (*c*) by the nature of the complicated attractive and repulsive force fields produced by the electrons and protons. The nature of these forces and the way in which they influence apparent diameters, condensation, and adsorption, have been indicated. Certain types of molecules have been discussed as examples of molecular structure. With these pictures before us, we can next proceed to see how these molecules will behave if left to themselves under temperature conditions where the mutual forces of attraction play a minor rôle. This study will complete the description of the nature of a gas which is essential to any later study of electrical conduction in gases.

II. THE KINETIC PICTURE OF A GAS*

7. The Avogadro Number.—As was stated in the introduction, the early chemical results leading to the law of constant and multiple proportions induced Dalton to revive an old Greek hypothesis that matter was composed of individual units, or building-stones, the atoms, of which now we have some ninety-two with distinct chemical properties. Each of these ninety-two consists of from two to four or more atoms of different atomic weights, the isotopes, whose weights are, however, fairly near together. A study of gas reactions led Gay-Lussac to postulate that atoms might constitute the units of which a gas was composed. Avogadro later clarified this hypothesis by assuming that while some of the particles could be individual atoms, others were *molecules* or *combined groups* of a few atoms, moving about as single units. He added the hypothesis that, if Gay-Lussac's results were to be interpreted by the molecular picture, equal volumes of gases at the same temperature and pressure must have the same number of molecules. The volume occupied by the atomic or molecular weight of a gas in grams must, therefore, be the same for all gases at the same temperature and pressure. This volume turned out to be 22.41 liters at 0° C. and one atmosphere of pressure, and this law of volumes was found to hold for all gases *once the proper atomic or molecular weight was assigned to the gas*. The number of molecules or atoms in 22.41 liters was therefore a constant of nature, and is called the *Avogadro number*. The numerical value of this number is about 6.064×10^{23} molecules. The number of molecules in a cm³ of gas is a definite fraction of the Avogadro number, and is often called the Loschmidt num-

* General References 10 and 12.

ber. It is 2.705×10^{19} molecules per cm³. As a result of recent studies on the kinetic theory of gases, the Avogadro number has been calculated or measured by some seven or more independent methods, and the value found is the same, to within the limits of the accuracy of measurement.

Some of the methods used are as follows: From the Faraday constant ($N_A e$) for electrolysis, knowing the valency of the ions and the charge e on the ions, N_A , the Avogadro number, can be computed. Millikan (7) measured e for electrons, and Rutherford (R 16) measured e for the α particles with a double positive charge. The values obtained agree within experimental errors. From the Brownian movements of colloidal particles, and from a study of the distribution of such particles in the earth's gravitational field, Perrin estimated N_A with considerable success (10 Chapter 8; R 17). From the kinetic theory of gases, we have a relation that the average distance gone over by a gas molecule between impacts is given by:

$$L = 1/(\sqrt{2\pi}\sigma^2 N) \quad (20)$$

where N is the Loschmidt number and σ the diameter of a molecule. L can be computed from the coefficient of viscosity of a gas, and σ can be obtained from the density of packed molecules in a liquid, or from the factor b of Van der Waals' equation for a real gas (10 Chapters 3 and 5). This gives satisfactory values for N . N could be directly computed from the volume production of He from α particles of radium during a year, and a measurement of the number of α particles given out by radium in a year (R 16). It can also be estimated from the rate of decay of radium, and the number of α particles given out by a given mass of radium in a second (R 16). These measurements are not accurate, but agree well.

The blue color of the sky depends on the molecular scattering of sunlight, and this equation involves a knowledge of the Avogadro number. As a result of actual measurements of molecular scattering, N_A was also determined

(R 18). Again, the energy of agitation or heat motion of a single molecule at an absolute temperature of T° C is given by the product $1.5 kT$, where k is called the Boltzmann constant. Since $1.5 N_A kT$ is the heat content of a gram molecule of a monatomic gas at T° absolute, any measurement giving k and T will give N_A . Now, k can be nicely evaluated by means of the Planck radiation laws for a black body, so that we can obtain N_A (R 19). N_A enters into certain quantum theory terms involved in the fine structure of some spectra (R 20). From the Sommerfeld theory of the atom and the accurate spectroscopic data, N_A can be evaluated. Finally with X-rays, we can accurately measure the wavelength of the X-rays on ruled gratings at grazing incidence. Then, by means of the X-rays, we can determine the distances between the atoms of a crystal such as rock salt. Knowing the density of the crystal and the molecular weight, the number of atoms of Na in a given crystal can be calculated with great precision (9, R 21).

The value now accepted for the Avogadro number is $(6.064 \pm .006) \times 10^{23}$ molecules per 22.4141 ± 0.0008 liters, or about 2.705×10^{19} molecules per cm^3 . We may thus assume that we know to some precision the value of this important constant.

8. Joule's Law.—Following the discovery of the mechanical equivalent of heat, Joule made an attempt at explaining the heat put into a gas as being expressed by the change in the kinetic energy of the gas molecules. In attempting to discuss this question, Joule first attempted to see whether the pressure of a gas could be explained by assuming the gas to be made up of molecules of average velocity c , and mass m . His elementary investigation yielded the simple and generally accepted equation:

$$\begin{aligned} pV &= (1/3)nmc^2 \quad (a) \\ \text{or} \\ p &= (1/3)Nmc^2 \quad (b) \end{aligned} \qquad (21)$$

where

- v = the specific volume;
- p = the pressure;
- n = the number of molecules in v ;
- $N = n/v$ (see 10 Chapter 2).

This equation proved to be a great step in advance, for it gave quantitative data which one could check. From it, we see at once that:

(22)

As Nm is the density ρ of the gas:

$$c = \sqrt{3p/\rho} \quad (23)$$

Evaluation of c , the average velocity of the gas molecules for various gases, follows at once, for any values of p and ρ . Thus for H_2 at $0^\circ C$ and 760 mm pressure, c is 1.839×10^5 cm/sec., while for nitrogen, under the same conditions, c is 4.93×10^4 cm/sec. This value is quite high, for this velocity is comparable with that of a fast rifle bullet. That the velocity is not unreasonable is shown by the fact that the velocity of sound is given by:

(24)

where γ is the ratio of the specific heats, that is, 1.66 to 1.00 for different gases, and we know sound to be carried by the molecules.

Since $c = \sqrt{3p/\rho}$, the velocity of the molecules may be shown to be independent of the pressure of the gas, though this velocity is responsible for the pressure exerted. If p is reduced to $1/2$, the density ρ is likewise reduced to $1/2$, so that c is, as a whole, independent of p . The velocity c is, however, distinctly dependent on the mass of the molecules, for since $\rho = Nm$, c is proportional to $1/\sqrt{m}$. Hence the molecular velocity is inversely proportional to the square root of the mass of the molecules, or the molec-

ular weight. Since the molecular weight of H_2 is 2 and that of Hg is 200, $c_{Hg} = c_{H_2} \sqrt{2/200} = 1.84 \times 10^4$ cm/sec. For electrons whose mass is $1/3720$ of that of the H_2 molecule, $c = c_{H_2} \sqrt{3720} = 1.125 \times 10^7$ cm/sec. Finally, the molecular velocity is dependent on the absolute temperature. This follows, since

$$pv = RT = (1/3)nmc^2 \quad (a)$$

hence

(25)

$$p = (R/v)T = (1/3)Nm c^2 \quad (b)$$

Thus (R/v) is the gas constant for the unit volume, and T is the absolute temperature. Hence, while the density Nm is kept constant, we see that c^2 is proportional to T , or c is proportional to \sqrt{T} . We can thus calculate the molecular velocity at any temperature T from the expression:

$$c_T = c_{273} \cdot \quad (26)$$

where the values above for c were those corresponding to 273° absolute, or 0° C.

One more important consequence follows from Joule's law. Since $pv = (1/3)nmc^2 = RT$, and since the kinetic energy of translation of a single molecule is $(1/2)mc^2$, and that of the n molecules in the volume v , is $(1/2)nmc^2 = KE$, it is clear that:

$$RT = (2/3)KE \quad (27)$$

That is, RT represents two-thirds of the energy of translation of the molecules at the temperature T° absolute for the n molecules for which R is chosen. Hence temperature, multiplied by R , accounts for *two-thirds of the kinetic energy of translation of the molecules*. This at once tells us that, as Joule suspected, when we compress a gas, the work of compression goes to increasing the energy of translation of the molecules, and the heat of compression is merely an expression of the increase in energy of the

molecules by the process. Hence a logical explanation of Joule's mechanical equivalent of heat and a description of heat in mechanical terms is achieved. This description may be quite logically carried over to the appearance of heat in all bodies, as an increase of the molecular energy of agitation of that body.

9. Equipartition of Energy.—In applying Joule's law, certain simplifying assumptions were made, including the assumption that the energy went entirely into the kinetic energy of *translation* of the molecules. In general this assumption is not true, and a discussion of the other types of mechanical molecular motion into which heat can go must be reserved for a discussion of specific heats. If we regard a mixture of two simple gases, having only translatory molecular motion, in equal volumes v_1 and v_2 , at the same temperature and pressure, we can write for each gas:

$$\begin{aligned} (R_1 T_1/v_1) &= p_1 = (1/3) N_1 m_1 c_1^2 \quad (a) \\ (R_2 T_2/v_2) &= p_2 = (1/3) N_2 m_2 c_2^2 \quad (b) \end{aligned} \quad \left. \right\} \quad (28)$$

Since by assumption $p_1 = p_2$ we can write $N_1 m_1 c_1^2 = N_2 m_2 c_2^2$. Since by Avogadro's rule, $N_1 = N_2$, we see that:

$$(1/2)m_1 c_1^2 = (1/2)m_2 c_2^2 \quad (29)$$

In other words, the average kinetic energy, KE_1 , of the one type of gas molecules, equals the average kinetic energy, KE_2 , of the other type of gas molecules. This is a statement of the theorem of the equipartition of energy among the molecules which is one of the fundamental theorems of the kinetic theory of gases. It is essential in most of our considerations, and is extended to the point where we assume that, while individual molecules may differ widely in velocities, *on the average, given enough molecules, not only are the average energies equal, but the energies are divided equally along the three axes of translatory motion; and where rotations occur, each degree of freedom of rotation shares equally in the distribution.* Actually,

while the theorem seems simple and obvious, there is no certain mathematical proof of its correctness, inasmuch as, in all proofs, there is a suspicion that the element to be proven is introduced in the assumptions necessary to the proof. Practically, the law of equipartition holds experimentally in a large number of cases, but appears to be limited by a new set of conditions, called the quantum conditions, of which more will be said later. At present, we shall tacitly assume its validity.

10. Mean Free Path.—Having now seen that this behavior of a gas may be explained by assuming it to be made of a large number of molecules, undergoing rapid motions of translation, proportional to \sqrt{T} , and inversely proportional to the \sqrt{m} , we must proceed further in our study of the picture of a gas. In doing so, we at once meet an *apparent paradox* with our assumptions as to molecular velocities. If a gas molecule moves with the speed of a rifle bullet, why is it that, when a bottle of ammonia is opened in one corner of a room, we do not immediately smell ammonia all over the room? This question caused a great deal of scorn to be heaped on Joule's theory. The situation was, however, relieved by the mathematical physicist Clausius, in 1857, through the introduction of a new concept (10 Chapter 3), that of free paths and collisions. Clausius assumed that, since we cannot see gas molecules, they must be very small, certainly a minute fraction of a wavelength of light in diameter, that is to say, at most they must be smaller than 10^{-6} cm. In such an event, to give the gas pressures observed, there must be a great number N of such molecules in a cm^3 . Since the molecules are not vanishingly small, they must occupy, with their large numbers, a not negligible fraction of the space in the cm^3 of gas containing the N molecules. He thus conceived of the straight-line paths of the molecules, moving with the velocity of a rifle bullet, as being very much interrupted by impacts with other molecules; thus, with the tortuous paths covered, even at a high speed, a molecule could not

very rapidly progress from the place from which it started. To analyze the situation, Clausius calculated the average distance which a molecule could travel in a straight line between successive impacts with other molecules, after which it experienced a change in direction. This average distance is termed the *mean free path* of the molecule or ion. It is clear that this path must depend on the numbers and sizes of the molecules concerned.

If we should picture a gas composed of idealized spherical molecules of diameter σ in which the density of molecules was N per cm^3 , we could picture the situation as shown in Fig. 4. It is seen that if the molecule A moved along AB , it would collide with the molecule B , in a short distance, while, if it moved along AC , it would go a considerable distance before colliding. In some other directions it could collide only after a still longer path, while in others, the collision would occur more promptly. If we consider that all the space about the molecule is ultimately hemmed in by the surfaces of other molecules, we see that eventually, no matter how A moved, it would collide and change its direction. Thus a molecule, A , is surrounded at each instant by a very complex, irregular, and moving surface, composed of the surfaces of other molecules, with which it may collide. Now since at each instant the chance of motion in any direction is equally probable, we see that there is a hope of calculating the average path before collision, provided the sizes of the molecules and their density are known. This Clausius calculated in direct manner from the picture we have just presented. The rather elaborate calculation need not be presented, and can be replaced by the following elementary deduction which gives the same result.

Assume all the N molecules per cm^3 to be fixed in space, and consider only one molecule moving with a velocity c . If we could straighten out the path of this molecule, its path, in one second, would be represented by a straight line c cm long (Fig. 5). Now, if the *center* of any other

similar molecule lies within the molecular diameter σ of the path of the moving molecule, it will suffer an impact with the

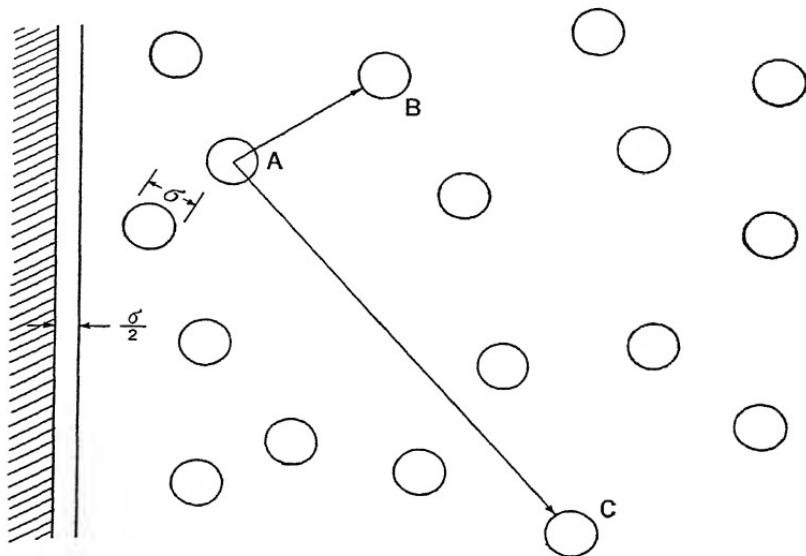


FIG. 4.—The Concept of the Free Path in a Gas.

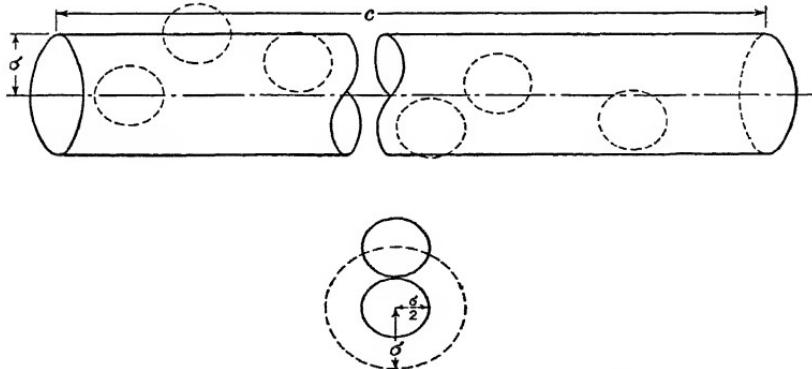


FIG. 5.—The Simple Derivation for the Value of the Mean Free Path.

moving molecule, for when the molecular centers are at σ perpendicular to the line of motion, there will be grazing

impact at the surfaces. If the distance is less than σ , the impact will be more nearly head on. Hence if a cylinder of radius σ and base area $\pi\sigma^2$ be drawn about the straightened path of the moving molecule, as an axis, this cylinder will include the volume for which every molecular center which lies within it represents a molecule with which the moving molecule will collide. The volume of the cylinder is $\pi\sigma^2c$ cm³. On the average, such a cylinder contains $\pi\sigma^2Nc$ molecules, for there are N molecules per cm³. Thus in one second, the moving molecule has $\pi\sigma^2Nc$ impacts. It covers a distance c cm in this second. Hence the average distance between impacts is:

$$L = c/(\pi\sigma^2Nc) = 1/(\pi\sigma^2N) \quad (30)$$

Had all molecules been moving with the same velocity, c , the value of L would have been slightly decreased, and more accurate calculation gives:

$$L = 3/(4\pi N\sigma^2) \quad (31)$$

Actually the molecules do not all move with the same velocity, and for the true distribution of velocities among the molecules, Maxwell has deduced the expression:

$$L = 1/(\sqrt{2}\pi\sigma^2N) \quad (32)$$

This expression is fairly accurate, but Tait has shown that in the process of averaging, Maxwell should have used a slightly more accurate procedure. The complex calculations lead to a value of L about 5 per cent higher than Maxwell's value. For the accuracy of most gas kinetic measurements, however, the Maxwell expression suffices, and it is the one generally used.

It is seen at once that the average distance covered between impacts depends chiefly on the number of molecules per unit volume and on the square of the molecular diameter, i.e., the molecular area of cross section. If σ is constant with temperature, which is nearly the case, and if the density is constant, that is, N is constant, it is seen

that L is independent of temperature, while, if temperature is constant, L varies as $(1/N)$ or inversely as the pressure of the gas. In other words, L is proportional to $(1/\rho)$ where ρ is the density, but is independent of T . This mean free path or average distance covered by the molecules between impacts is an exceedingly important concept for a study of the electrical behavior of gases. It is perhaps the most important type of parameter entering into such studies. The question of the value of L may now appropriately be raised. As shown in the study of atomic structure, the diameter of an atom is of the order of 10^{-8} cm. The diameters of molecules are somewhat larger and, when we get to molecules of substances like the proteins, they may reach dimensions of nearly 10^{-6} cm. In gases, generally, we deal with diameters of some 4×10^{-8} cm. At 760 mm. pressure and 0°C (or N.T.P.), the Loschmidt number, N , is 2.7×10^{19} ; hence, we can at once calculate L as follows:

$$\begin{aligned} L &= 1/(3.14 \times 1.41 \times 2.7 \times 10^{19} \times 16 \times 10^{-16}) \\ &= 5.2 \times 10^{-6} \text{ cm} \end{aligned} \quad (33)$$

or in general, of the order of about 10^{-5} cm, which is the value for air.

It is to be noted that the mean free path calculated is the *average* distance between successive impacts of a given molecule. It is obvious, however, that this is *not the length of the individual paths*, which, as shown in Fig. 4, are sometimes long and sometimes short. It is therefore of importance to determine the way in which the individual free paths are grouped about this average value. In other words, it is going to be of considerable interest and importance for us to know what the chance is that a molecule will have, either a path of a given length, or a path which exceeds a given length. Again, it will be important to know what fraction of the paths of a given molecule will exceed a certain path under given conditions.

It is seen from the nature of the free path concept, based on Fig. 4, that the probability of a free path of length x depends, beyond the number and size of the molecules which give the average value, only on the chance that a molecule moves in a given direction. It is thus purely a chance phenomenon. On this assumption, it is easy to calculate the *chance of a free path*. The result of a relatively simple calculation is that out of n_0 molecules starting a path at a given instant, or out of a total of n_0 paths experienced by a given molecule, the number, n , which exceed a distance x , is given by

$$n = n_0 e^{-(x/L)} \quad (34)$$

where L is the average, or mean free path. This relation is easily visualized by plotting the ratio of n/n_0 as ordi-

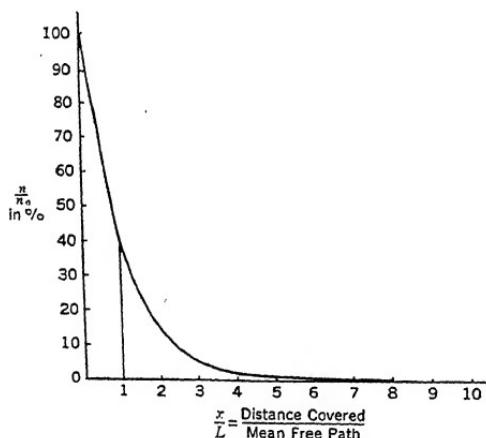


FIG. 6.—The Distribution of Free Paths.

tion of the paths which exceed the mean free path L , in length. The curve has no maximum, and the paths have all lengths, the longer paths becoming fewer in number. The mean free path is thus merely the *average* of the exponential curve, and is in no sense a fixed or most probable path. Thus the mean free path, while a convenient

ordinates, against x , as abscissae, as shown in Fig. 6. The value of n/n_0 at $x = 0$ is 1.0. At $x = L$, $n/n_0 = 1/e$ or 0.3679. At $x = 2L$, it is 0.13534, and at $x = 5L$, it is 0.00674. It is thus seen that the number of paths of length x rapidly drops, for paths greater than $2L$, to small values. The value of n/n_0 at $x = L$, gives the frac-

average value, cannot and should not be considered in an absolute sense. Again, no matter what the value of L , the distribution is of a constant form, and L acts as a sort of numerical scale factor, determining the number of paths exceeding a given x . L is determined by the nature of the molecules and their number. The function is, however, exceedingly useful in problems of discharge through gases, for the reason that electrons and ions, while moving over free paths, are subjected to the free actions of the electrical fields, and the energies acquired from the fields between impacts determine what will occur at the next impact with molecules or surfaces.

It is essential to realize that while

$$n/n_0 = e^{-(x/L)} \quad (35)$$

gives the fraction of the paths exceeding x , it does not tell how many molecules will collide within a given distance, dx . To do this, we must differentiate n with respect to x . Hence the fraction of molecules colliding between x and $x+dx$ is given by

$$(dn/n_0) = (-1/L)e^{-(x/L)} dx \quad (36)$$

The minus sign indicating that dn/n_0 decreases as x increases.

For most qualitative calculations in evaluating orders of magnitude, the mean free path may be used to determine what will happen. If, however, more accurate values are needed, it is best to include the distribution of the free paths in the calculations, and integrate between zero and infinity. To illustrate the order of magnitude of the errors to be expected by disregarding the distribution, and using the mean free path alone, we can state that in the simple theory of ionic velocities in unit field, the use of the mean free path gives a value for the mobility of the ion of:

$$k = (1/2) (e/m) (L/c) \quad (37)$$

While if we take into account the distribution of the paths in a very simple manner, the expression becomes:

$$k = (e/m) (L/c) \quad (38)$$

That is to say, the use of the *distribution* gives a value twice as great.

The reality of the distribution of the free paths has been established and the evaluation of the mean free path has been accomplished over a great range of free paths and velocities for electrons, by direct experiment. It has also been carried out for a more limited range of free paths for silver atoms in nitrogen gas, by direct methods, so that we are fairly certain of our fundamental facts. The values of the mean free paths of some molecules, among molecules of their own kind, have been obtained from data on the transport phenomena, such as diffusion, heat conduction, and viscosity in gases. The best values of these come from measurements of viscosity, where there are less inaccuracies in measurement and theory. The free paths can also be computed, if we know the values of σ , the molecular diameters, and N_A , the Avagadro number. As the latter is well known, it requires only a knowledge of σ . This can be obtained from data such as Van der Waals' b (10 Chapter 5) obtained from the Joule-Thomson effect, or from the critical temperature data. Since, however, σ as determined by different methods (as stated in the discussion of molecular diameters and force fields) has different values which depend on an interpretation of the meaning of σ , these values must be used with caution, where accuracy is desired, especially because L varies as $1/\sigma^2$ (see Eq. 32).

For the case of N_1 molecules of diameter σ_1 per cm^3 , moving in a gas of N_2 molecules per cm^3 , of diameter σ_2 , L has a value L_{12} different from that for molecules of diameter σ_1 , in a gas composed of its own molecules. The slight correction must be taken account of if we deal with

ions moving in a gas where the ionic radius is greater than that of the molecules. The exact expression is:

$$L_{12} = 1 / [\sqrt{2\pi N_1 \sigma_1^2 + \pi N_2 \sigma_a^2 \sqrt{(c_1^2 + c_2^2) / c_1}}] \quad (39)$$

where

$$\sigma_a = (\sigma_1 + \sigma_2) / 2 \quad (40)$$

and c_1 and c_2 are the velocities of the molecules of subscripts 1 and 2, respectively. The first term in the denominator deals with collisions between the σ_1 molecules themselves, and the second term with those between the σ_1 and σ_2 molecules. For ions where N_1 is small, this first term can be neglected. It may be further pointed out that, since the number of impacts per unit time, and hence the mean free path, is a function of the velocity of the molecules, the mean free path will vary slightly with the velocity of the molecules. The exact expression has been worked out by Tait and is very complex. It is hardly of importance in the rather inaccurate and crude experiments dealing with electrical discharge phenomena.

For convenience, a table of common mean free paths is included at the end of this text (see Appendix II).

11. Molecular Velocities.—In the first part of this text, the molecular velocities were calculated to be of the order of magnitude of fast rifle bullets, but little was said of the velocities of individual molecules, as only average values for a large number of molecules in a volume, v , were calculated. It is now necessary to discuss the values of velocities of individual molecules more in detail (10 Chapter 4). The idea that molecules are perfectly elastic in their impacts (necessitated by the specific heat relations and the fundamental kinetic theory) leads at once to a definite prediction about the velocities of individual molecules. Consider two equal molecules starting off with equal velocities and striking each other with their initial paths at right angles. The molecule struck moves off with the resultant velocity of the two velocities at right angles,

while the molecule striking, if the impact be perfectly elastic, is brought to rest. Hence, while before impact, each molecule had a velocity c and a kinetic energy $(1/2)mc^2$, after impact, the struck molecule has a velocity at 45° with the initial motion of value $c\sqrt{2}$, and the other molecule has a velocity 0. The energy of the two, however, remains constant, for the energy is now:

$$W = (1/2)m(\sqrt{2}c)^2 + (1/2)m(0)^2 = mc^2 \quad (41)$$

While this is a relatively rare type of impact, it is clear that all sorts of redistributions of velocities and energy will take place after the first impact for a large group of molecules starting with the same velocities at a given instant. As a result of such collisions, there will be a complete distribution of velocities at any instant in the gas, in which some molecules will have a velocity near 0, while others, as a result of several cumulative encounters, may have 4 or more times the initial or average velocity.

For elastic impacts, the *average* energy and hence velocity, per molecule, remains constant. It is important therefore, to determine, if possible, what this distribution is, and how many molecules out of a given number have a certain fraction of the velocity corresponding to the average energy. This can be done by making certain assumptions. The first is that we are dealing with a large number of molecules, for if we dealt with only a few molecules, the velocities at any instant would be few in number, and not representative. It is further essential that the molecules should have been colliding for a time long enough so that they have reached their state of equilibrium. Adding to these postulates the assumption of perfectly elastic impacts, and assuming for simplicity spherical molecules, Boltzman calculated the distribution of velocities among the molecules on the basis of the equilibrium conditions which must ensue. The calculations are exceedingly complex, but the distribution law found agrees very well with that deduced independently by Maxwell on purely statistical grounds.

The results of these calculations in the form in which they are most frequently used in calculations involved in the breakdown of gases will be given.

The limited number of molecules, N_{dc} (10 Sections 34 and 35), having velocities between c and $c + dc$ out of an assemblage of N molecules, is given by:

$$N_{dc} = [4N/(\alpha^3\sqrt{\pi})]\epsilon^{-(c^2/\alpha^2)}c^2dc \quad (42)$$

This relation can be visualized by plotting N_{dc}/N as ordinates, against the value of c , in terms of α , as abscissae. The curve obtained, for $dc/\alpha = 0.1$, is shown in Fig. 7. It will be noticed that

at $c = 0$ and $c = \infty$, the ratio N_{dc}/N becomes = 0. In between N_{dc}/N rises to a maximum in a sort of an unsymmetrical bell-shaped curve. The maximum of the curve occurs at $c = \alpha$. Hence α is the most probable velocity of the molecules, i.e., the velocity most frequently found. If we calculated the average velocity, we would find that, owing to the slightly greater preponderance of the higher velocities, the average velocity lies at the point \bar{c} on the curve whose value is:

$$\bar{c} = (2\alpha/\sqrt{\pi}) = 1.128\alpha \quad (43)$$

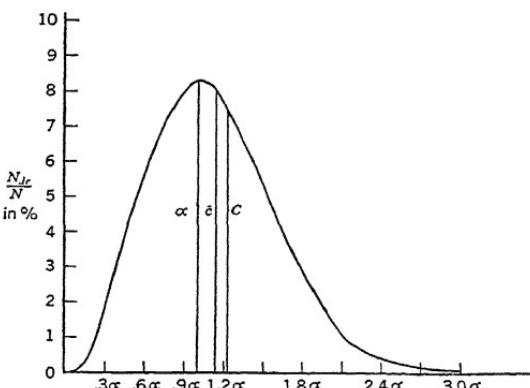


FIG. 7.—The Distribution of Molecular Velocities.

In evaluating the velocity of the molecules above, we found this velocity to be equal to the quantity $\sqrt{3p/\rho}$. We note that the velocity so obtained is really the square root of an average of the squared velocity, that is:

$$\bar{c}^2 = 3p/\rho \quad (44)$$

whence we have a quantity $\sqrt{c^2}$. Even if the curve were symmetrical, such a square root of the average squared velocity would not be the same as the average velocity, for in squaring numbers, averaging them and extracting the square root of the average, the larger numbers are given a greater weight.*

The value of $\sqrt{c^2}$ is given by:

$$C = \sqrt{c^2} = \sqrt{(3/2)\alpha} = 1.224\alpha \quad (45)$$

Hence, in the studies of gases, we have to consider three velocities, namely, the most probable velocity α , the average velocity c , and the square root of the average squared velocities or the effective velocity C . These are related as follows:

$$\alpha : \bar{c} : C = 1 : (2/\sqrt{\pi}) : \sqrt{3/2} = 1 : 1.128 : 1.224 \quad (46)$$

and the ratio of \bar{c} to C is:

$$\sqrt{8/3\pi} = 0.922 \quad (47)$$

In addition to these velocities whose relations must be known to interpret different experimental data, one may point out that observation may require still other averages to be known. Thus in a beam of atoms coming from a slit in a hot oven, since the number escaping is the greater, the faster the molecules, the average velocity is distinctly higher than the average velocity of the molecules corresponding to the temperature of the furnace. In this case, the square root of the average squared velocity, C_1 , of the stream relative to the square root of the average squared velocity in the furnace, will be given by:

$$C_1 = \sqrt{4/3}C \quad (48)$$

In describing the distribution of molecular velocities, another form of representation is sometimes used, and the

* This is analogous to the distinction between the average and the effective value of an a.c. voltage.

frequent occurrence of this form in the literature requires that this form and certain other common representations of the distribution law be given.

Eq. 42 applies to molecules moving in all directions. If it is desired to describe the motions of the molecules along some three coordinate axes, x , y , and z , in terms of separate component velocities u , v , and w , along these axes, we can write that the number of molecules having velocity components between u and $u + du$ along x , v and $v + dv$ along y , and w and $w + dw$ along z , are:

$$\begin{aligned} N_{du} &= N(1/\alpha\sqrt{\pi})e^{-(u^2/\alpha^2)}du \\ N_{dv} &= N(1/\alpha\sqrt{\pi})e^{-(v^2/\alpha^2)}dv \\ N_{dw} &= N(1/\alpha\sqrt{\pi})e^{-(w^2/\alpha^2)}dw \end{aligned} \quad (49)$$

while the probabilities of velocity components u , v , and w separately corresponding to the above conditions are:

$$\begin{aligned} f(u) &= (1/\alpha\sqrt{\pi})e^{-(u^2/\alpha^2)} \\ f(v) &= (1/\alpha\sqrt{\pi})e^{-(v^2/\alpha^2)} \\ f(w) &= (1/\alpha\sqrt{\pi})e^{-(w^2/\alpha^2)} \end{aligned} \quad (50)$$

The simultaneous chance that a molecule will have velocities lying between u and $u + du$, v and $v + dv$, w and $w + dw$, is:

$$\begin{aligned} f(u) f(v) f(w) du dv dw = \\ (N/\alpha^3\pi^{3/2})e^{-(u^2+v^2+w^2)/\alpha^2} du dv dw \end{aligned} \quad (51)$$

Again we have a relation:

$$pv = (1/3)nmC^2 = RT \quad (52)$$

$$(mC^2/2) = (3/2)(R/n)T = (3/2)kT \quad (53)$$

Boltzmann designated the gas constant R divided by the number n of molecules, that is, the *gas constant per molecule*, by the letter k . This is known as the Boltzmann

constant, and is continually used in the literature. Hence, the average kinetic energy of a molecule is:

$$(1/2)mC^2 = (3/2)kT \quad (54)$$

Therefore:

$$C = \sqrt{3kT/m} \quad (55)$$

and since

$$\left. \begin{array}{l} C = \sqrt{(3/2)\alpha} \quad (a) \\ \alpha = \sqrt{2kT/m} \quad (b) \end{array} \right\} \quad (56)$$

We can write the distribution law as:

$$N_{de} = 4\pi N(m/2\pi kT)^{3/2} c^2 e^{-(mc^2/2kT)} dc \quad (57)$$

This law really gives the distribution of kinetic energy among the molecules for a gas at a temperature T . Through the extension of the ideas of equilibrium in a gaseous system by the law of equipartition of energy, this law may be still further carried to any system in equilibrium in the form of the expression that the number of molecules having an energy between E and $E + dE$ in such a system is given by:

$$N_{dE} = ND e^{-E/kT} dE \quad (58)$$

Where D is an appropriate constant. Finally, since we wrote that the number of molecules having velocity components along x , lying between u and $u + du$, was given by:

$$N_{du} = N(1/\alpha\sqrt{\pi})e^{-u^2/\alpha^2} du \quad (59)$$

and since

$$C^2 = 3kT/m \quad (60)$$

and if we call

$$h = 1/2kT \quad (61)$$

we obtain

$$C^2 = (3/2)mh \quad (62)$$

Moreover,

$$C^2 = (3/2)\alpha^2 \quad (63)$$

and hence

$$\alpha = \sqrt{1/mh} \quad (64)$$

so that

$$N_{du} = N(hm/\pi)^{\frac{3}{2}} e^{-hmu^2} du \quad (65)$$

For all three components along x , y , and z , simultaneously, we have:

$$N_{du\ dv\ dw} = N(hm/\pi)^{\frac{3}{2}} e^{-hm(u^2+v^2+w^2)} du\ dv\ dw \quad (66)$$

while for the molecules with velocities between c and $c + dc$, we have:

$$N_{dc} = 4\pi N(hm/\pi)^{\frac{3}{2}} c^2 e^{-hmc^2} dc \quad (67)$$

All these various forms are in constant use in papers which have bearing on various gaseous problems and are here reproduced for handy reference or comparison.

This so-called Maxwell-Boltzmann distribution of velocities among the molecules is of great importance in many considerations. It is seen that, unlike the free paths, the molecular velocities are in the main clustered pretty closely around a most probable value. Thus a very small number of molecules have twice the most probable velocity, while a still smaller number have five times the most probable velocity. The exponential nature of the curve has, moreover, an important function. For suppose that at a certain velocity, or energy of impact, molecules could collide violently enough to dissociate each other. If *all* the molecules had the *same energy and velocity*, dissociation would appear abruptly when the temperature was reached at which the molecules had the requisite energy and velocity. With the distribution law, however, the situation is quite different. Already at one-third of the absolute temperature requisite for the dissociation, a minute but appreciable fraction of the molecules have velocities which cause them to dissociate, and at 0.65 or so, of the requisite temperature, some one-sixth or more of the molecules will suffer dissociating impacts. Hence phenomena depending on the

attainment of energies of a certain value will actually occur gradually and not abruptly as the temperature rises. Thus, for instance, in the case of evaporation of molecules from a liquid surface, the evaporating molecule must gain kinetic energy sufficient to escape from the surface. Consequently, there is an evaporation of a noticeable amount, far below the temperature at which the average molecule can escape. The vapor pressure curve for a substance has thus an exponential form with increasing temperature. The shape of this curve can accurately be deduced from the kinetic theory by the use of the law of distribution of velocities among the molecules and the known work of removing molecules from the surface, that is, the latent heat of vaporization (10 pp. 319 ff.). In fact, one of the finest experimental verifications of the Maxwell-Boltzmann law of distribution of velocities among particles in thermal equilibrium is derived from a measurement of the velocities with which electrons are liberated from an incandescent metal. Since the velocity of an electron can easily be accurately measured by electrical means, the velocities of the electrons in thermal equilibrium with an incandescent metal surface have been measured by Germer (10 Section 45) over a range of temperatures within which the number of electrons varies in the ratio of 1 to 10^{10} ; the numbers so observed have been found to obey the Maxwell distribution law within the observable limits of error. A direct verification of the law has also been made by means of a direct measurement of the velocities of molecules, using rapidly rotating discs or sectors (10 Section 44).

12. The Law of Equipartition of Energy.—It has been stated that a generalization of the law of distribution of velocities contained the implication that the energies are equally distributed among the molecules (10 Section 36, also Chapter 9). That is, that given a large enough number of molecules, the average energy of any group of molecules is the same as that of any other group and is characteristic of the absolute temperature of the gas. This law can be

even more generalized as follows. If we regard the translatory motions alone (in the case of atomic units), the energy of motion along any one of the three coordinate axes is the same as that along any of the other two axes. For if the gas is in equilibrium, with no streaming motion, the motion along any one axis is just as probable as along any of the other axes. Since we have the simple equation $RT = (2/3)KE$, where KE is the kinetic energy of motion of all the molecules, we see that $(3/2)RT = KE$. If we assume that the energy along the three axes is equally distributed along the axes, the *average KE* along *any one axis of translation* is $(1/2)RT$. If we take the value of the kinetic energy for an interval of temperature dT , that is, if we differentiate the expression above, we have:

$$(3/2)RdT = d(KE) \quad (68)$$

And for one axis:

$$(1/2)RdT = d(KE) \quad (69)$$

That is, $(1/2)RdT$ is the change in the kinetic energy of translation along a single axis of motion. Since R is nearly 2 calories per gram molecule, and if $dT = 1^\circ C$, we see that the change in KE along any axis for 1° change in temperature is roughly 1 calorie.* The three axes of motion in translation are the only independent directions of motion possible. We call the various independent motions possible the *degrees of freedom* of motion (10 Chapter 9). Hence, we can state the law of equipartition of energy more generally by saying that for 1° change in temperature per gram molecule, there is, due to equipartition, 1 calorie of heat absorbed per degree of freedom of motion. This generalization at once permits us to consider the more complicated cases, where the molecules can rotate, i.e., possess other degrees of freedom of motion.

*Actually, the deviation is less than 1 per cent, because $R = 1.98$ calories per degree, and this is equal to 2, within the accuracy of most specific heat measurements in engineering practice.

Let us consider first the motion of the simplest molecule, which consists of two massive atomic centers at the ends of a line joining the two. In such a system, it is simpler to analyze the complex molecular motion as a motion of translation of the *common center of gravity* of the two atoms, and a rotation of the two atoms about this center. In such a molecule a simple analysis shows that besides the three degrees of freedom of motion of translation of the center of gravity, the two molecular centers (i.e., masses practically concentrated at the nucleus) can rotate about two axes at right angles to the long axis of the molecule (i.e., at right angles to the line of centers). The spin of the molecules about the line of centers we can for the present neglect, as the masses of the two atoms lie on the line and the moment of inertia of the molecule about this line is nearly zero. Hence for a diatomic molecule, there are three degrees of freedom of translation and two of rotation, or five degrees of freedom of motion in all. Equipartition demands that each of these degrees of freedom absorb 1 calorie per degree rise in temperature per mol of gas, or that the molecular heat, $d(KE)/dT$, for such a molecule be 5 calories, compared to the value of 3 calories for the atomic heat for a monatomic mass point, or an atom. This follows, since $d(KE)$ for 1° difference in temperature is nothing but the specific heat of a gas at constant volume per gram molecule or the molecular heat.

For a tri- or polyatomic molecule, there are three degrees of freedom of translation of the center of gravity of the molecule possible, and there are three degrees of freedom of rotation about the common center of gravity. This makes a total of six degrees of freedom of motion, so that for a triatomic, or polyatomic molecule, there are, in general, 6 calories involved in a change of $1^\circ C$ at constant volume. Hence the molecular heat of a polyatomic gas at constant volume is 6 calories.

If we consider the specific heat at constant pressure for any gas, we must remember that besides increasing

the temperature, the heat causes the gas to do an external work equivalent to $p dv$, where p is the pressure, and dv the change in volume due to expansion against p . If in such a gas we neglect the internal work of expansion, we can write, at a constant pressure for a gram molecule:

$$pdv = RdT \quad (70)$$

We thus see that, due to external work done, there must be about $R = 2$ calories per mol per degree rise in temperature added for the work of expansion. Hence, in all cases above discussed, the specific heat at constant pressure, C_p , is 2 calories per degree per mol (for R is taken per mol) greater than the specific heat at constant volume, C_v .

We can summarize all these facts by saying that, if equipartition demands equality of energy distribution among the degrees of freedom of motion at the rate of 1 calorie per mol per degree rise in temperature, the molecular or atomic heat of a gas must take on the values as follows for the different cases cited; thus:

C_v for a monatomic gas, 3 degrees of freedom (translation) = 3 calories.

C_v for a diatomic gas, 5 degrees of freedom (2 rotation, 3 translation) = 5 calories.

C_v for a polyatomic gas, 6 degrees of freedom (3 rotation, 3 translation) = 6 calories.

C_p for a monatomic gas, 3 degrees of freedom + external work = 5 calories.

C_p for a diatomic gas, 5 degrees of freedom + external work = 7 calories.

C_p for a polyatomic gas, 6 degrees of freedom + external work = 8 calories.

Hence:

$$\gamma = C_p/C_v \text{ for a monatomic gas} = 5/3 = 1.666 \quad (a)$$

$$\gamma = C_p/C_v \text{ for a diatomic gas} = 7/5 = 1.40 \quad (b) \quad \left. \right\} \quad (71)$$

$$\gamma = C_p/C_v \text{ for a polyatomic gas} = 8/6 = 1.33 \quad (c)$$

A preliminary survey showed that, in general, the values predicted above for the molecular specific heats, or specific heats per mol, were given correctly by the law of equipartition. There were, however, glaring exceptions to be noted, such as in the cases of Cl_2 and Br_2 , where the values of C_v were more nearly 6 and 7 for these diatomic gases, instead of 5. Again, gases like ether and many others showed values of C_v distinctly greater than 6 and values of γ much less than 1.33, while H_2 at low temperatures has $C_p = 5$, instead of 7. The explanation of these deviations was at first not evident, and the derivation of the law of equipartition was subjected to much more critical analysis, to see whether the difficulty might lie in a flaw in the deduction of the law. The results obtained, however, were inconclusive. It remained for a new physical principle to be discovered and applied to this study before the meaning of these deviations became clear (10 p. 367 ff.). This was the principle of quantum action, which more truly governs discharge and atomic phenomena than any other principle.

Before proceeding further, it might be worth while to look at another type of motion possible in molecules of the diatomic or polyatomic type which we have ignored. This is the oscillatory motion of atomic centers towards each other, due to disturbances of the atoms of molecules in impact. From a study of the molecular structure already given, we have seen that it is to be expected that the atoms found in a molecule should undergo *oscillatory motions relative to each other*, i.e., the atoms of a molecule may vibrate back and forth, relative to the center of gravity of the molecule. Or again, in a crystal, the atoms or molecular units are elastically bound by electrical forces, and vibratory heat motions of these must be possible—witness the transfer of sound and heat waves through a crystal.

One may well ask what the law of equipartition demands of the energy distribution in such a system being capable of executing periodic heat vibrations. The answer is com-

paratively simple. In an oscillating system, Bernoulli long ago showed that the energy was in part kinetic and in part potential, and that, in general, the average energy involved in motion equaled the energy involved in displacement, relative to the elastic forces (i.e., one-half the energy was kinetic and one-half of it was potential). Hence, equipartition would at once ascribe to each degree of freedom of vibration, two calories of energy per degree per mol, as the energy must be equally distributed among the potential and kinetic phases of motion. Thus, if Br_2 had one degree of freedom of vibration active, 2 calories should be added to C_v , making $C_v = 7$ calories, instead of 5. Again for an elastic solid crystal, having three degrees of freedom of vibration per atom possible along the three axes for a mol of crystal per degree centigrade, the molecular or specific heat per mol should be 6 calories. For atomic crystal lattices, this was found to be the case (law of Dulong and Petit) as long as the temperature was high enough for all substances, and provided the temperature did not become too high. At temperatures below 0°C ., the values of C_v for these atomic crystal lattices rapidly decreased, approaching 0 at absolute zero, and at different rates for different substances. Thus, again, the law of equipartition appeared to be well substantiated within certain limits, but there were always notable exceptions.

It is therefore possible at this point to raise another question, that is, why, if C_v for solids can be accounted for on the elastic vibrations of the atoms, the gases like H_2 , N_2 , and O_2 , as well as some other gases, do not have values of C_v universally higher by 2 or more calories, due to the vibratory motions of the atoms in the molecules? Again, another question hitherto lightly passed over may well be raised. After all, the electrons in the outer portions of monatomic and diatomic gases do add a small but real mass at considerable distances from the centers of the atoms. These masses have finite although small moments of inertia. Hence they can have energies of spin, and C_v

for monatomic gases might well, therefore, be 6 calories instead of 3, due to the spinning of the electron shells about the nuclei. Finally, one may ask how it happens that atomic or molecular impacts are elastic at all, in view of the fact that the outer electron shells and force fields are primarily concerned in molecular impacts, so that these also should share in the equipartition of energy.

It seems surprising, therefore, that while the principle of equipartition is understandable, and apparently sensible, it should not be actually applicable in the simple form observed for a large number of molecules. Closer analysis shows that the above simple formulation neglects such important complicating factors as electronic vibrations, outer electronic spin, and atomic vibrations in molecules with all their additional degrees of freedom, which should enter into the picture and complicate it (10 p. 370 ff.; 4 Chapter 8). The simplicity of the law must mean that, besides the law of equipartition of energy, there is another law of very wide applicability, which limits the degree to which equipartition may be active in many cases.

This law appeared for the first time in an apparently unrelated phenomenon, i.e., that of the radiation laws. In 1900, Max Planck showed that in order to derive the radiation laws for hot bodies as a function of the wavelength of the emitted radiation and the temperature, the vibrators emitting radiation in incandescent solids could not be capable of absorbing and emitting equally all wavelengths in any amounts, but that a vibrator of frequency ν could only absorb or emit energy in multiples of a given unit. This unit he showed must be given by $h\nu$, where h was a new universal constant of value 5.65×10^{-27} ergs secs., and ν was the frequency of the radiation involved. For references to this see 4 Chapter 7; and 5 Chapter 3.

Very quickly this idea was transferred to the question of specific heats by Nernst, Lindemann, and Einstein, so that already by 1908, the deviations from Dulong and Petit's law of atomic heats at low temperatures were quite

successfully explained on this principle, and the limitations of the law of equipartition by the quantum principle, as it was called, was indicated for the case of the gases (4 Chapter 8). The quantum principle, as applicable to the problem in question, may be stated as follows: Given any periodic function of time in molecular phenomena, i.e., rotation, vibration, or spin, then, if the frequency be designated by the symbol ν , the degree of freedom of motion having the characteristic frequency ν can share in the equipartition of energy only when in the course of energy transfer the processes are able to give the vibrator quanta of energy in an amount $h\nu$ or multiples thereof, in a single act. That is, unless a molecular impact can give a vibrating atom in a chlorine molecule having a natural frequency ν , an amount of energy equal to $n h\nu$, where n is an integer, the degree of freedom of vibration cannot be awakened, and take part in equipartition, i.e., that degree of freedom can be regarded as "dormant." The quantum theory, therefore, sets a definite limit to the law of equipartition by saying that equipartition can hold only when the energy given at an impact is as great as or greater than the minimum energy characteristic of the particular mode of vibration or periodic motion involved.

Since, in thermal phenomena, the energy of impact is distributed according to the Maxwell-Boltzmann law, i.e., there is a considerable range of energies of impact present at any given temperature, the *appearance of a particular mode of energy absorption as the temperature is raised is not abrupt at the value:*

$$(1/2)mv^2 = kT = h\nu \quad (72)$$

but begins well before this energy is reached for a few of the molecules, and increases in frequency of occurrence gradually to nearly universal application to all molecules, as the average energy exceeds the value $h\nu$.

This quantum limitation explains at once why, in all gases, no energy goes into electronic vibrations at ordi-

nary temperatures (10 Section 91). For at room temperatures, the energy of agitation is of the order of 5.617×10^{-14} ergs for a single molecule (at 0° C). The energy required to excite the first of the yellow sodium lines, which involves one of the lower electron excitation energies, is 3.37×10^{-12} ergs. Hence the energy to excite the electrons of sodium to light emission is some 60 times that of agitation at room temperatures, so that scarcely 1 atom of the 2.7×10^{19} in a cm^3 of Na vapor would be excited, even if it could be held at this density at room temperature. In fact, the Na vapor must be at a temperature of some 900° C or more before the energy of impact is sufficient to make the D lines of Na appear. At 1000° C, the average energy at impact of atoms corresponds to 2.22×10^{-13} ergs, and under these conditions, only a fraction (1.3×10^{-13}) of the atoms colliding, get an energy not much exceeding that to make the Na vapor glow, i.e., an energy equivalent to 4.77×10^{-12} ergs.

Again, when we consider the spin of the outer electron shells of atoms, or of diatomic molecules about the nucleus, we find that the energy causing such a spin of the outer shell of an atom, due to the low moment of inertia of the electrons and the high frequency of the spin, is of the order of 10^{-11} ergs. Hence we can see that the specific heats for atoms and molecules are kept at the smaller values, ignoring such things as electron excitation to light emission and spin of the outer shells, in spite of equipartition, by the laws of quantum action.

When we come to consider the question of the energy of vibration of the atoms in a molecule along the lines of juncture, the situation is modified by the fact that for some molecules this energy is relatively low. Thus, for instance, while the dissociation energy (i.e., that to cause vibration of the molecules great enough to split the atoms apart) is 6.94×10^{-12} ergs for H_2 , 1.43×10^{-11} ergs for N_2 , and 9.15×10^{-12} ergs for O_2 ; it is only 3.95×10^{-12} ergs for Cl_2 , 3.1×10^{-12} ergs for Br_2 and 2.61×10^{-12}

ergs for I_2 . Hence, since the energies involved in vibration are about one-tenth (or even less) of those involved in dissociation, it is to be expected that appreciable numbers of the Cl_2 , Br_2 and I_2 molecules should be excited to vibration even at $0^\circ C$. This, in fact, is shown to be the case, as seen by the infra-red absorption spectra of these gases which show quite marked absorption of light corresponding to the various degrees of vibration present. Thus for many gases, such as Cl_2 , etc., which are readily reactive chemically, because of loose binding of the atoms in the molecule, we should expect to find degrees of freedom of vibration taking roughly 2 calories per degree present, and indicated by the high values of the specific heats observed.

As the frequencies ν of rotation of the molecules are much lower than those of vibration, we should expect at ordinary temperatures to see all gases possessing their full quota of rotational energy and manifesting them in their molecular heats. This in fact, is true. It was predicted that for H_2 , because of the rotational frequency ν being the highest and the substance being a gas at very low temperatures, the H_2 molecule with its low moment of inertia should have a value of ν such that at 90° absolute (the temperature of liquid air) the rotations of the H_2 molecule should no longer exist. Thus, at this temperature, C_v for H_2 should be 3 calories, C_p should be 5 calories, and γ should be 1.66 (i.e., at 90° absolute, H_2 should act as a monatomic gas). At 270° absolute C_v should be 5 calories, C_p should be 7 calories, and $\gamma = 1.40$ (i.e., H_2 should act as a diatomic gas). This has been completely confirmed by experiment by Eucken and by Cornish and Eastman (10 p. 372). The transition is a gradual one between these temperatures, as is to be expected from the distribution law; the curve observed for MC_p (molal heat capacity) as a function of the absolute temperature is shown in Fig. 8.

The same behavior with temperature is to be observed

in the case of crystalline atomic lattices (10 Sections 93 and 94: 4 Chapter 8). As the temperature decreases towards 0° absolute, at first a few, later most, and finally all the degrees of freedom of vibration freeze up, and MC_v for crystals drops to zero at absolute zero along curves quite analogous to the type of curve observed for H_2 . The theoretical values have been computed by Einstein, Nernst and Lindemann, and finally by Debye. These values are in accurate accord with observation. From the theory and observations, ν , the characteristic frequencies

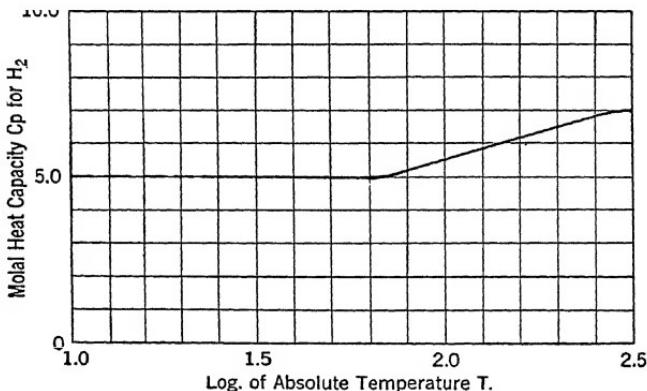


FIG. 8.—Molal Heat Capacity at Constant Pressure for H_2 as a Function of Absolute Temperature.

of atomic vibration, have been computed for various substances and agree with those calculated or determined by optical observations. The elements Si, C and B, which have the highest known melting-points, have the highest values of ν for any elements. For these substances we do not get all vibrations "active" until temperatures of 900° C. or more are reached, when MC_v is observed to reach 6 calories per gram-molecule. For other crystalline solids it has been found that MC_v is not 6 times the number of atoms present in the molecules. However, MC_v is constant for various molecular groupings, for example, NO_3 , CO_3 ,

SO_4 , S, combined with atoms. This indicates that, among the molecular groupings, some of the atoms are bound so tightly that at room temperatures the atoms in a group cannot vibrate, and the groups at least in part vibrate as a unit. At higher temperatures MC_v for all these increases, as one might expect.

The conclusion of this discussion is that in general for each degree of freedom of translatory or rotatory motion in general, 1 calorie of heat per mol is absorbed by a substance per degree rise in temperature. In some cases of vibratory motion, the vibrations partake of equipartition, and 2 calories must be added per degree of freedom per degree centigrade per mol for each such degree of freedom. The equipartition is governed by the fact that unless the average energy of motion (i.e., the temperature of the molecules) is such that a considerable proportion of the impacts result in energy transfers exceeding the quantum $h\nu$, where ν is the characteristic frequency of some periodic process, rotation or vibration, that particular degree of freedom remains inactive and is not involved in equipartition. All transitions from inactivity in equipartition to activity and sharing of energy, as temperature increases, must be gradual, on account of the law of distribution of energies among the molecules.

Apropos of the question of energy of agitation, temperature, and the law of equipartition, a very important caution should be given. This is, that all the processes discussed under this heading are assumed to be equilibrium processes. The laws of equipartition and of detailed balancing, of Klein and Rosseland (R 22), to be discussed later, all require *enough particles, freedom from outside energy gains, energy gains or losses, and sufficient time to achieve a complete chaos*, or "mixed-upness" of energies. Now in many physical processes, especially in the discharge through gases and other dielectrics, heating and other effects are being produced electrically and the temptation is to carry over the simple kinetic concepts applicable

to equilibrium to these cases. In a neon lamp, or glow discharge, the color of the light emitted would indicate that the gas in the tube was at a temperature of at least the order of 1000° C. A thermocouple or thermometer, placed in the discharge, shows that this is entirely incorrect. What is occurring is that, by means of an electrical field, electrons which rebound quite elastically, losing less than 10^{-4} of their kinetic energy in impacts with the gas atoms, are selectively acted on by the field and are given enough energy to remove selectively electrons from neon atoms or to disturb the electrons in neon atoms, so as to give rise to light emission. The kinetic energy of the electrons in the tube is thus selectively very high, i.e., *the electrons have a high "temperature," while the neon atoms and positive ions have only a temperature of some 50 to 100°*. Indeed, the low inertia of electrons does not permit them to transfer much energy to massive atoms. This is, therefore, in no sense an equilibrium process, inasmuch as the light from the neon is radiated out as fast as the electrons excite its atoms, and the energy does not go to the atoms, for the excitation is selectively by electrons acted on by the field. This fact is often forgotten by physicists and engineers. It is dangerous to attribute a temperature on the basis of light radiated, unless one knows that the radiation really represents a temperature equilibrium.

A typical example of such faulty reasoning lies in a theory which attributes spark breakdown in gases to a process of temperature ionization. It is possible and even probable that, if the energy of molecules or atoms were increased to a high enough value, these could ionize each other. Saha (13 p. 191 ff.; R 23) and others have in fact worked out a thermodynamic theory for such a process, assuming equipartition and ionization by molecular impact. A proof of this condition is difficult, as regards mechanism, in that when such temperatures are reached in the absence of chemical processes (such as in flames, e.g., in an electric furnace), there are always large numbers of high-

energy electrons in thermal equilibrium with molecules which could do all the ionizing. In the case of spark breakdown, after the breakdown occurs, the ionization found is of the order of magnitude of that to be expected from a temperature ionization produced by the temperature observed. However, in spark discharge, all *this energy comes from the action of the high fields on electrons and positive ions, and not from neutral molecules in equilibrium.* Hence it is not correct to interpret the mechanism of spark discharge on the basis of a phenomenon reached after the spark has passed, that is, due to a selective electrical effect which is by far not an equilibrium process.

One may, with a summary of the foregoing material, profitably leave the discussion of the kinetic picture of a gas as sufficiently complete to give an essential background for the study of the electrical conduction in gases.

13. Summary.—From what has been described before, it is clear that atoms consist of a nucleus of minute size composed of electrons, protons, and α particles. This nucleus comprises most of the mass of the atom, having a positive charge Z equal to the serial number of the element in the periodic system. The nucleus is furthermore inviolable as regards ordinary physical and chemical processes, owing to the high energy involved. Surrounding this nucleus are Z electrons arranged in groups or levels characterized by the energy necessary to disturb them and by quantum conditions. These electrons are also minute, compared to atomic dimensions, being, at most, 10^{-4} of the atomic diameters. The electron levels or shells are characterized by the numbers of electrons in them, and as long as Z is great enough, each shell is complete. The stable types of groupings of electrons characterizing the shells are given by the paired electrons or the octette, as shown by the external structure of the inert gases. In striving to complete their outermost shell of electrons, in conformity with principles of stability illustrated by the inert gas group, the atoms will form chemical combinations.

Such combinations are called molecules. Inasmuch as, even with electrical neutrality, the complex atomic and molecular electrical structures have residual electrical force fields, these fields will interact with each other on the approach of atoms or molecules. At greater distances, these forces of interaction are predominately attractive, and of an inverse third to fifth power type. At distances comparable with (and actually defining) the atomic or molecular diameters, the forces are largely repulsive, and of an inverse seventh to an inverse eleventh power form. It is the interactions of these force fields between atoms and molecules that give the order of magnitude of the apparent atomic and molecular radii, and must vary as the energies and nature of the molecules change.

In the gaseous state, molecules move with an average velocity proportional to \sqrt{T} and inversely proportional to \sqrt{m} , which is of the order of that of rifle bullets or the velocity of sound in the gas. These motions are continuous and eternal as long as the temperature is maintained constant. Besides these motions of translation of molecules at lower temperatures, the molecules rotate about axes (at most three in number) and vibrate along lines of centers of the component atoms. At lower temperatures, because of quantum restrictions, these motions may cease and only translation remain. At 0° absolute, *theoretically*, all motions should cease. Actually, the bodies are all in the solid state, and in this state they have an energy which is technically called the zero point energy, which is near but not equal to zero. At higher temperatures the energies under proper conditions may remove the quantum restrictions, and the spin of the outer electron shells as well as energy jumps of electrons may take place, causing radiation of light.

In this whirling, vibrating, and darting motion of the molecules and atoms of a gas, the molecules and atoms suffer "collisions" with each other; that is, they come together to within distances at which interactions of their electrical force fields are such as to cause the particles to

deviate markedly from the straight-line paths which they would normally pursue in vacuo. In such changes of direction, there are also energy exchanges following the laws of momentum and energy. If the temperature is high and the gas not too dense, the paths will be straight up to within nearly 10^{-7} cm of the particles struck. As the temperature decreases and attractive forces begin to predominate, the potential energies at the average distance of separation approach the kinetic energies of heat motion of the molecules, and the paths become more and more curved. Since the energies are distributed over a wide range of values, all sorts of impacts and paths will occur at any given time, and transitions from straight paths to curved ones will be gradual as temperatures decrease. This gradual transition, due to energy distribution following Maxwell's law, will apply as well to transitions required by quantum restrictions as otherwise.

The distance which a given molecule will traverse as a straight line between any two encounters is governed entirely by chance, but at any given temperature and pressure, for a given molecule in a given gas, the average value of this distance has a definite value called the mean free path. The latter depends for its value, as previously indicated, on the density of the gas and the so-called apparent diameter of the molecules. This apparent diameter is defined by an equation which says:

$$L = 1/(\sqrt{2\pi}N\sigma^2) \quad (73)$$

Where σ is this apparent diameter, or one-half the sum of the diameters of the colliding molecules. A graphical instantaneous picture of a small portion of gas, enlarged 10^6 times, is shown in Fig. 9.

By lowering the temperature to a point where the average potential energy of the molecules (due to attractive forces) is greater than the average kinetic energy of the gas molecules, the gas condenses. That is, the orbits of the molecules, cease to be straight for distances of the order

of the average distances between the atoms, and are continually curved. The molecules or atoms thus describe orbits about each other, or better about their common center of gravity, and they are said to have "captured" each other. In the chaotic state of such motion, the orbits interlace each other in a most complicated fashion. Under these conditions, the substance cannot expand to fill any vessel, and we have a liquid. In the process of contracting

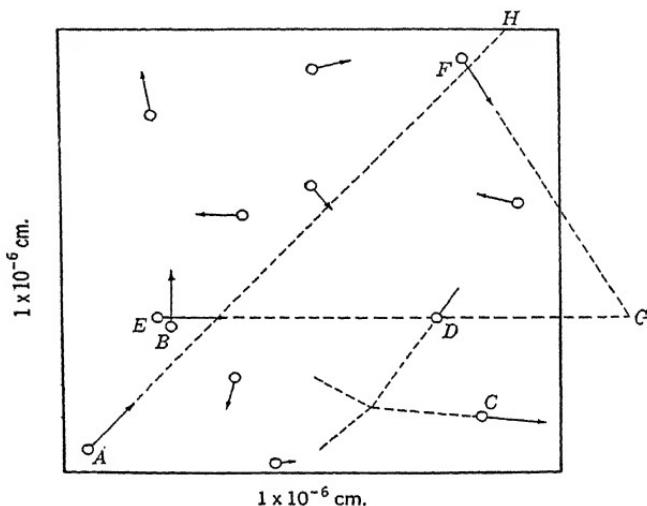


FIG. 9.—Idealized Instantaneous Picture of a Gas Magnified 0.6×10^7 Times.

One mean free path is a path such as one given by AH , ten times the length of this square. Molecules E and B are just missing a collision. Molecules C and D have just collided. Molecule E is one of the rare molecules to collide with another molecule F in a path ending at about $\frac{1}{10}$ of the average free path (less than 10% of the molecules collide in this distance). 0.6 cm length of arrow indicates a velocity of 400 m/sec.

to gain the state of closed orbits, the potential energy due to attractive forces is dissipated, and this, together with the work due to pressure times change of volume, constitutes the latent heat of condensation which is liberated in the process. In other words, molecules so "capture" each other that they cannot easily escape from their neighbors and so fill any volume. In this state, however, as

soon as a molecule gets energy from the Maxwell-Boltzmann distribution, which enables it to escape from a free surface of the substance, on a long free path, against the attractive forces, it leaves the surface and thus evaporates.

As the kinetic energy becomes still lower, the molecules and atoms are still further hampered in their motions relative to the other molecules and atoms of the liquid. Here the lack of symmetry of the force fields (they are not spherically symmetrical, as stated before) comes into play, and a very slow molecule or atom will find that it has not sufficient energy to escape from a particular region of a similar atom or molecule which it has approached. It in turn will "capture" and hold another molecule in an appropriate region, and so the substance takes on an ordered solid structure in three dimensions of space, i.e., in a crystalline space lattice. Here the molecules or atoms are held in position by powerful oriented forces, leading to the crystalline symmetry, and the only heat motion which such bodies show is a vibrational one along certain restricted directions. When a molecule in a lattice receives an especially violent jar from other neighboring molecules in the crystal or from outside molecules, it may gain enough kinetic energy to escape and leave the solid either as a gas molecule (subliming), or as a molecule ready to execute the motions characteristic of the liquid state. As in the case of condensation, the change in potential energy from the liquid to the crystalline state, together with the work of expansion or contraction on solidification, is called a *latent* heat which is designated as that of fusion.

It must be continually borne in mind, however, that the changes described are all covered over by the statistical nature of the processes involved, i.e., by the Maxwell-Boltzmann law, and we can speak of only the average behavior. In the detailed processes of condensation and of solidification, however, other processes may come in. Thus, in condensation, it often happens that before the liquid state is reached, many molecules form groups of two

or more molecules quite a while before condensation, and in the liquid state quite a while before solidification; we then have groups of associated molecules. Both effects are observed. Thus certain of the alkali metal vapors before condensation will form diatomic molecules, and water in saturated steam forms such groups, or nuclei of condensation, sometimes of large size, which have been observed by Barus and others. In the liquid state polar molecules, such as H_2O and alcohols, are highly associated in groups.

Possibly a word might also be said at this point about the dielectric properties of gases and liquids (15 Chapters 2 and 3). Many molecules, as stated, are polar in nature, for instance, NH_3 , H_2O , $\text{C}_6\text{H}_5\text{NO}_2$, and others. In the gaseous state, owing to the low density of such gases and vapors, the dielectric constant is low. This constant is further lowered by the violent heat motions which serve to *disorient* the molecules in an electric field. As the substance condenses, the dipoles are concentrated into 10^{-4} of the former volume, and heat motions are far less violent. Again association plays a great rôle, and we find dielectric constants of the order of 81, 35, and 14, instead of values of 1.0027, for these substances. In liquids, any free ions such as Na^+ and Cl^- , from dissolving NaCl , are immediately surrounded by a labile group of polar molecules which protect them from ions of the opposite signs and prevents or retards recombination. In gases, however, the effect is far less, owing to higher energies and greater distances of separation. Thus in aqueous and other solutions, ions can exist freely, while in gases the ions eventually recombine. In solids, the polar molecules are largely set into the crystal lattice as ions to begin with. On fusion or softening of the crystal, some of these get loose, and, at adequate temperatures, we find many crystals becoming ionic conductors.

The above picture of the gaseous state, in its relation to the other states of matter and to temperature, furnishes

a good qualitative picture of a gas to guide one in a study of the electrical behavior of gases. While the data and descriptions given may seem rather speculative and somewhat artificial, considering the actual size of molecules, we can, however, state that practically all of the essential points have been verified experimentally to a high degree of precision and rather directly. Even the unceasing erratic heat motions of the gas molecules have been more or less directly observed and quantitatively verified through the beautiful work of Millikan and Fletcher on the Brownian movements of oil drops. With this statement we can safely leave the description of the gas and turn to a study of the electrical disturbances which atoms and molecules undergo and which are termed ionization and excitation processes.

III. IONIZATION PHENOMENA

14. General Considerations.—So far a picture has been given of the electrical structure of atoms and molecules and the general behavior of these units in gases under normal conditions. It is, however, well known that when these units of matter are acted on by situations causing considerable energy transfer to them, they are disturbed from their normal electrical states. It is now necessary to consider the conditions causing such disturbances, the laws governing them, and the nature and extent of the disturbances produced.

The general picture of the normal electrical atomic and molecular configurations, postulated by Bohr and adequately expressed by quantum and wave mechanics formulations, is known to depend on energy relations between electrical charges. Therefore, it is at once evident that any disturbance of the energy relations, by transfer of energy to the electrons by other electrified bodies or electromagnetic waves, must alter the structures in some fashion. For the usual energy conditions encountered, one can at once rule out changes in the nuclei in considerations which we are about to discuss as these require energy concentrations on single charges which cannot at present be achieved by man, and are observed very rarely, even with high-energy radioactive decay products. Again, a second limitation can at once be imposed on all such disturbances on the basis of the fact that Bohr's formulation of atomic structures postulates the application of quantum conditions (2 p. 4 ff.). This means that no atom or molecule can be perturbed from its normal state by any sort of disturbing agent, unless that agent by some mechanism can confer on the portion of the atom or molecule disturbed, enough

energy (within the limited time of its interaction) to give some portion of the configuration at least one quantum of energy. The quantum is determined by the value of the energy involved in the return to the normal state, which is $h\nu$, where ν is the frequency of the particular energy to be emitted on the return.

We can further frankly admit complete ignorance of any adequate mechanical picture of the processes of energy transfer, for, as has been stated before, the gross mechanics of Newton is unable to account for the behavior of atomic configurations. Thus, it is now necessary to attempt to discover the relations between atoms, electrons, and light quanta, and by this means to formulate the facts in terms of a new system of concepts, instead of attempting to picture them from a Newtonian viewpoint. In fact, for the simple phenomena involved in hydrogen-like atoms, the new wave mechanics can mathematically adequately describe atomic and molecular behavior (5 Chapters 15, 16, and 18). Eventually, it may be possible to extend this to other simple structures also (5 Chapter 19). Too much of the "how" of the processes to be described can, however, hardly be looked for, and we must content ourselves with the bare facts. At times, for the sake of visualization, we will treat problems from the more classical mechanical point of view. These pictures must be regarded, however, with caution, and serve only to guide the thinking.

The first great step made in the study of what happens to gaseous atoms and molecules was due to Franck and Hertz in 1913 (14 Chapter 2; 5 Chapter 3, Section 11, Chapter 13; 23 Part 1; 24 Chapter 9). By actual experiment, they discovered that when beams of electrons, emitted by a hot filament and accelerated in an electric field, were shot into gases like He, Hg, H₂, and N₂, at low pressures, so as to make but few collisions with the molecules or atoms before being analyzed, the electrons were reflected practically without loss of energy, unless they struck these atoms with an energy greater than a given

amount. In what follows, it will be convenient to express energies of electrons in terms of the difference of potential, V , through which they must be accelerated in free fall to give them the velocity and energy in question. From the equation:

$$(1/2)mv^2 = Ve \quad (74)$$

we can readily express the energy $(1/2)mv^2$ in terms of the equivalent volts V required to accelerate an electron (having a charge e) to a velocity v .

Hence, when we speak of electrons of V volts energy or velocity, we are really saying that the electrons have an energy $(1/2)mv^2$ equal to a potential difference V in volts, multiplied by the charge e on the electron. To give an idea of the magnitudes involved, a few values of v , $(1/2)mv^2$, and V are given below (22).

T °C *	v (cm/sec) *	$(1/2)mv^2$ (ergs) *	V volts *
0,000	1.125×10^7	5.617×10^{-14}	0.0359
7,457	5.94×10^7	1.591×10^{-12}	1.000
77,027	1.84×10^8	1.591×10^{-11}	10.000
772,700	5.94×10^8	1.591×10^{-10}	100.000

* T = temperature of the gas.

v = mean velocity of an electron in thermal equilibrium at the specified temperature.

$(1/2)mv^2$ = molecular kinetic energy.

V = energy in volts required to impart, to the electron, the specified velocity.

In the case of Hg atoms, for example, the value of V below which impacts were perfectly elastic, was found to be usually at 4.9 volts, and rarely at 4.66 volts, while for He it was more nearly 19.5 volts. For molecular gases, like N₂ and H₂, there appeared to be a slight loss in energy below the more critical values of 8.52 and 11.15 volts to be expected (R 24). At first these losses could not be explained, but the recent work of Harries (R 25) on N₂

and CO_2 shows that there are individual but infrequent losses in such gases below what are normally supposed to be the critical voltages. These can be accounted for by properties of molecules which atoms cannot possess, i.e., losses due to vibrations of the atoms in a molecule.

It was, of course, obvious that, even for perfectly elastic impacts between electrons and molecules, there was always a small but definite fractional loss of energy, f , for the electrons, resulting from their finite mass and the laws of conservation of mechanical energy and momentum. This fractional energy loss, f , has been computed for electron impacts with atoms from the laws of momentum and energy by K. T. Compton (R 26), and is as follows:

$$f = 2(m/M) [1 - (\Omega/u)] \quad (75)$$

where Ω is the average kinetic energy of the molecule or atom and u is the average energy of the electrons, while m is the mass of the electron and M that of the molecule. When (Ω/u) is small, f is fairly closely given by:

$$f = (2m/M) \quad (76)$$

Since $m = 8.99 \times 10^{-28}$, while $M = 1.65 \times 10^{-24} \times M'$ M' being the molecular weight of the molecule, f can be easily computed. It is seen that even for the lightest molecules f is of the order 2.17×10^{-3} . This law was also tested experimentally in the case of He, by Compton and Benade (R 26), and found to be correct. For N_2 and H_2 , the results indicated that the same relation probably held, but the results were disturbed by the occasional losses of energy due to single impacts below the recognized limit for elastic impacts in these gases.

The conclusion, therefore, is that in most gases electrons collide elastically, losing only a minute fraction, $f = (2m/M)$, of their energy in impact with molecules or atoms, provided that their energy lies below a certain critical value characteristic of each gas considered. For motions of electrons in gases, where electrons make but

few impacts with molecules, this loss can be neglected. It plays, however, an important rôle at higher pressures in many phenomena.

15. Critical Potentials.—The minimum values of the potentials at which definitely inelastic impacts of electrons with atoms or molecules set in, and where the electrons lose all or a large fraction of their energy at a single impact, are called *critical* potentials (5 Chapter 3, Section 11; 14 Chapter 2; 23 Part 1; 24 Chapter 9). It was at first observed that the conductivity of the gas was increased at the critical potentials, and these potentials were assumed to be the so-called ionization potentials of the atoms or molecules struck. That is, it was assumed that when an electron acquired an energy of V_0 equivalent volts characteristic of a given gas, it was able on impact to remove an electron from an atom whose ionization potential was V_0 .

The Bohr theory of spectral lines, however, indicated that an electron should be able to lose energy to an electron in an atom or molecule as soon as it possessed an energy equal to:

$$h\nu = (1/2)mv^2 \quad (77)$$

where ν was the frequency of the light radiated, when the disturbed electron returned from its excited orbit or state to its initial orbit or state. It was, therefore, suspected that the first inelastic impacts at increasing energies should correspond to these excitation losses leading to light emission, and not to ionization, the ionizing potentials being higher. Experiment definitely showed this fact to be true, and the increased conduction currents were proven to be a secondary phenomenon, due to photoelectrons (electrons liberated by light from the excited atoms) originating on the electrodes. It must be pointed out here that, in experimental work on ionization by various agents, great care must be taken to make sure that actual ionization of the gas is taking place and not a liberation of electrons from

metal parts of the chamber through the various agencies used.

It was found that, in complete conformity with Bohr's theory, the first inelastic impacts of electrons with atoms and molecules at lower energies in general gave rise to the emission of light of the first line of a given series of lines of these atoms, and that as the electron energies increased, the separate higher lines of appropriate ν appeared as the energy reached the proper value (5 p. 458 ff.; R 27). At the limit of a given spectral series, as the quantum numbers n of the orbit or state increase, the lines lie more and more closely together (2 Chapters 8 and 9; 5 p. 59 ff.; 4 Chapter 11). The electrons in the outer orbits or higher quantum states (corresponding to higher values of n) lie at greater and greater distances from the nuclei, and are correspondingly less and less tightly bound. Finally, at an appropriate energy of the impacting electrons, the atomic (or molecular) electrons are completely removed from the atoms (or molecules), leaving them positively ionized (atomic ions or molecular ions). When an electron possesses more than an ionizing amount of energy, any superfluous energy which it has after causing ionization is distributed between itself and some electrons removed from the atoms. In other words, such higher-energy electrons ionize atoms and molecules, and retain part of the energy left over or give it to the escaping electron. Nothing is accurately known about how this energy is distributed, as it is impossible to distinguish the initial ionizing electrons from those escaping from the atoms. The energies of impacts, or voltages, causing changes in electronic levels within the atoms are called *excitation*, *resonance* (really inappropriate on the original Bohr theory), or *radiation* potentials, whereas voltages corresponding to the energy of impacts which just suffice for ionization are called the *ionization* potentials. For instance, in He, electrons of 19.5 volts energy excite a metastable state (26 p. 96). On the other hand, it requires 21.12 volts to excite

the first line of the He series, and electrons of 24.5 volts energy ionize the He atom and produce an extra electron and He^+ .

16. Multiple Ionization, or Ionization and Excitation.—It appears possible that a single impact of an electron with appropriate energy upon an atom might at the same time liberate two or more electrons from the same atom, or ionize and excite the same atom, or even cause transitions of two different electrons in the same atom to higher states. Experimental evidence for and against these possibilities has been brought forward from time to time, but there have been until recently no conclusive proofs of such occurrences due to single electron impact. The most definite evidence lies in the recent work of Maxwell (R 28) and particularly Bleakney (R 29) who by positive ray analysis has shown that a single electron of appropriately high energy can liberate as many as four or five electrons at once from an atom as rich in outer electrons as Hg. The work on dissociation and the mechanism of ionization in certain gases such as N_2 , H_2 , and other gases by Smyth (R 30), Dempster (R 33), Kallmann (R 32), and by Hogness (R 31), as well as Franck (14 Chapters 7 and 8; 5 p. 461 ff.), has indicated the probability of the simultaneous excitation and ionization of the same atom by a single electron impact of appropriate energy. Some spectral evidence for the presence of the shift of two electrons to higher orbits by single electron impact was seen in what were termed double electron jumps, but this evidence has been questioned (R 34). Needless to say, the energy of electrons causing such multiple effects in a single atom must be considerably higher than for the single effects, and the probabilities of such events must in general be lower than for the single electron effects in a single atom or molecule. A table of values of these potentials for some well-known atoms and molecules is given in Table III.

In general, it can be stated that the ionization and resonance potentials of the inert gases are correspondingly

TABLE III
TABLE OF CRITICAL POTENTIALS IN VOLTS

Element	Atomic Number	First Exciting Potential	Metastable State	Ionization Potential	Second Ionization Potential
He.....	2	19.75	$\begin{cases} 19.73 \\ 20.55 \end{cases}$	24.48	54.16
Ne.....	10	16.60	21.47	
Ar.....	18	11.57	$\begin{cases} 15.69 \\ 15.86 \end{cases}$	
Kr.....	36	9.9	13.3	
Xe.....	54	8.3	11.5	
H.....	1	10.15	13.54	
Li.....	3	1.84	5.37	
Na.....	11	2.09	5.12	
K.....	19	1.60	4.32	
Rb.....	37	1.55	4.16	
Cs.....	55	1.38	3.88	
Mg.....	12	2.70	7.61	
Ca.....	20	1.89	6.08	
Hg.....	80	$\begin{cases} 4.66 \\ 4.89 \end{cases}$	(2537) 7.69	10.39	18.97

higher than for similar active elements in the same part of the periodic table. The lower potentials are usually found among the metallic elements of the first and second groups of the periodic table. It is also found, with a few exceptions, that the larger the diameters of the atoms and the larger the numbers of external electrons, the smaller the excitation and ionization potentials will be. Electrons of higher energy, such as those of the order of 100 volts, can also excite and ionize electrons lying in the inner shells of the atoms, giving rise to high-frequency ultra-violet radiations, or even soft X-rays, while energies in the thousands of volts can give rise to X-rays. The probabilities of such excitation and ionization by faster electrons are again, in general, lower than for excitation and ionization of the lower energy levels of the atoms, chiefly because of the fact that there are more of the lower energy electrons

TABLE III.—(*Continued*)

Gas	First Excitation Potential	Ionization Potential	Dissociation Potential
H ₂	11.15	15.3	4.36
N ₂	{ 8.52 9.47 }	16.7	{ 9.06 11.6 }?
O ₂	6.10	14.1	{ 7.05 6.5 }? 5.75
NO.....	5.44	9.4	{ 7.9 8.3 }?
CO.....	5.97	14.2	11.0
CO ₂	10.0	14.3	
H ₂ O.....	7.6	13.2	
Cl ₂	13.2	2.47
Br ₂	12.8	{ 1.96 2.00 }?
I ₂	2.3	10.1	{ 1.53 1.50 }?
NH ₃		11.1	
HCl.....	13.75	
HBr.....	13.25	
HI.....	12.75	
CH ₄	9.5	
C ₂ H ₂	9.9	
C ₂ H ₆	10.0	
CHCl ₃	6.5	11.5	

present in the atoms. However, when one attempts to discuss the mechanism of the processes (if this be allowed) it is observed that due to time factors occurring in the interactions, the faster electrons may react rather more selectively on the more rigidly bound electrons.

17. Mechanism of Ionization.—When one attempts to picture the process of ionization from a mechanical or electrodynamical viewpoint, one is hampered not only by the lack of knowledge of the mechanical behavior of the electrons in the atoms (for they do not in atoms obey Newton's laws) and by the mysterious quantum conditions which govern this action, but also by the great mathematical

complexity of the problem. Since electrical forces between charges are of an inverse-square-law type, the interactions of two moving charged particles (i.e., two electrons), free in space, can be easily computed by analogy to our well-known astronomical problems, with due regard to the sign. But even the case of a hydrogen atom (proton with one orbital electron and a bombarding electron of adequate energy) is the incompletely solved astronomical three-body problem. More complex structures are even less amenable to mathematical analysis. Furthermore, in all such calculations, the possible solution, based on considerations of electrodynamic disturbances, is complicated by the quantum restriction that an electron can receive energy only in case it can absorb a whole quantum from the disturbing charge in the process. It appears from the earlier chapters that the magnetic fields play a relatively small rôle in the cases of the more slowly moving charges, though for faster particles these forces must doubtless also be considered.

The simplest cases open to study, so far, have been the ionization by rapidly moving electrons (0.1 the velocity of light), or by α particles from radioactive atoms above certain velocities. Suppose one calculate the momentum given an atomic electron by such a charge ($mv = ft$), where f is the force and t the time over which it acts (impulse) from classical electrodynamics. One can then assume that an electron in the atom can be removed or excited only if it receives an energy $(1/2)mv^2$ equal to or greater than the ionizing energy or the $h\nu$ characteristic of the change it can undergo. Under these conditions, by calculating the distances over which electrons can obtain this energy (from a moving charge of given velocity), and knowing the number of electrons per unit volume of matter traversed at this distance, we arrive at a value for the number of ions produced and the loss of energy of the fast particles. The values so computed agree in order of magnitude with observation (R 35). The computed energy loss is, however, always less than the observed loss, by a factor of

the order of two or a bit more. This means that there are processes of energy loss not accounted for by the assumed mechanism which must be explained. This difficulty is analyzed on the same basis as the following problems which must first be stated. A difficulty is encountered from the classical point of view above, especially for charged massive bodies, such as α particles and protons unaccompanied by electrons. Such charges, according to the classical theory, have not high enough velocities to impart the ionizing energy to electrons on the basis of the laws of momentum and energy, unless they have velocities corresponding to a free fall of potential from 10,000 to 3,000 volts, on account of their great masses relative to those of the electrons (R 36). Yet such charged particles appear to ionize below these energies, albeit very inefficiently compared to the ionization above such energies. In the case of electrons, of course, the ionization by moving electrons takes place from the ionizing energy upwards. The reason for the ionization by slower positive ions, of velocities below 3,000 volts, is due, as the writer (R 36) has pointed out, to the fact that at lower velocities the α particles and protons have picked up an electron or two, and it is therefore not by virtue of the initial charge that these particles (at velocities below 10,000 and 3,000 volts) ionize, but they ionize by a new process dependent on the presence of the electrons. It accordingly must follow that even a neutral molecule can ionize another such molecule, provided it has enough energy. This fact is borne out in the processes of change of charge of α particles at the end of their range (R 37).

A third factor in ionization by more slowly moving particles is the complicated resonance effects which occur between electrons in an atom executing their movements in the Bohr orbits, if they can be so considered, and the time of passage of an external electron or charged particle in the neighborhood of the atom. These effects even on a classical mechanical theory can be expected to occur, but

are difficult to calculate (R 38; R 39). This action, as well as the other two phenomena discussed above, cannot receive an adequate explanation on any simple mechanical theory.

As time goes on, however, it becomes increasingly clear that there is much more coherence of the electrons in atoms, and in interaction between them, than one would be able to surmise on a simple classical mechanical analysis. Thus the work showing multiple ionization, and ionization and resonance by a single electron impact, indicates that by some process the energy of the one passing electron is redistributed by the electron ensemble of the atom as a whole in an effective way. Furthermore, the ionization by positive ions of low speed, and by neutral atoms or molecules, would also indicate that collisions between the multiple electronic atomic systems are such as to be able to transfer the translatory energy of ionization possessed by the atom or ion as a whole to one particular electron which is excited or removed (R 36). These processes are apparently very much less probable than processes in which a single electron interacts with a single electron of the atom, but they do occur, and, while not characterized by any clear mechanism, are of great importance in discharge phenomena.

While as yet the new so-called wave mechanics * has hardly been applied to the consideration of processes of ionization, except in simple hydrogen-like atoms, these applications indicate that the wave mechanics can accurately predict the behavior, where it has been applied (R 39). Needless to say, the analysis of these processes, while adequately represented by the equations, finds no simple Newtonian mechanical analogue or picture. This is not surprising, since we are here dealing with generalizations of our Newtonian mechanics for which we have no simple picture. These facts indicate that while to date

* Strictly speaking, the new formulation termed "wave mechanics" is not really mechanics at all, for the term mechanics implies the use of Newtonian formulations which do not apply here.

the complete and accurate treatment for ionization of more complex atoms by the "wave mechanics" has not been achieved, owing to mathematical difficulties, we are hopeful of a description of the mysterious process above mentioned, in a coherent, logical, and accurate scheme, by means of the so-called wave mechanics.

18. Probabilities of Ionization and Excitation.—When we regard the quantitative results of the ionization by electron or other impact, as well as excitation, we find that not every electron ionizes or excites *as soon as it has the requisite energy*. In fact, the efficiency of the processes is rather low. That is, using impacts defined by the kinetic theory between a moving electron with ionizing energy, or greater energy, and atoms or molecules, we find that many impacts can occur before ionization takes place. The same holds also for exciting impacts. Many attempts have been made to measure the probability of ionization or excitation on this basis. The difficulties encountered lie largely in the fact that as soon as the first excitation potential, or the first ionization potential, is reached, subsequent increases in energy cause the second, the third, etc., steps to occur, and they are difficult to separate. The difficulty is increased since the electrons used in experiments do not, in general, all have the same energy, but owing to the nature of their origin, i.e., from a hot filament, etc., have quite a diverse set of energies which are superimposed on the energy given by the field. These cause overlapping of the effects of the many excitation potentials which characterize an atom and complicate the result. A typical example of better results, obtained by recent observers, is seen in the excellent curves of Compton and Van Voorhis (R 40) and of Bleakney (R 29), shown in Figs. 10 and 11. Lawrence (R 41), by segregating electrons of a unitary velocity with a magnetic field, obtained a more detailed picture of the processes (5 p. 476 ff.). According to this work, the probability of resonance or ionization is greatest at the precise ionizing or resonance potential, and falls off exponen-

tially from that value on, only to rise again as the next potential is reached. An integration of such curves, over different potentials, gives the type of curve obtained by Compton and Van Voorhis. The work of Lawrence, although apparently convincing, is not generally accepted,

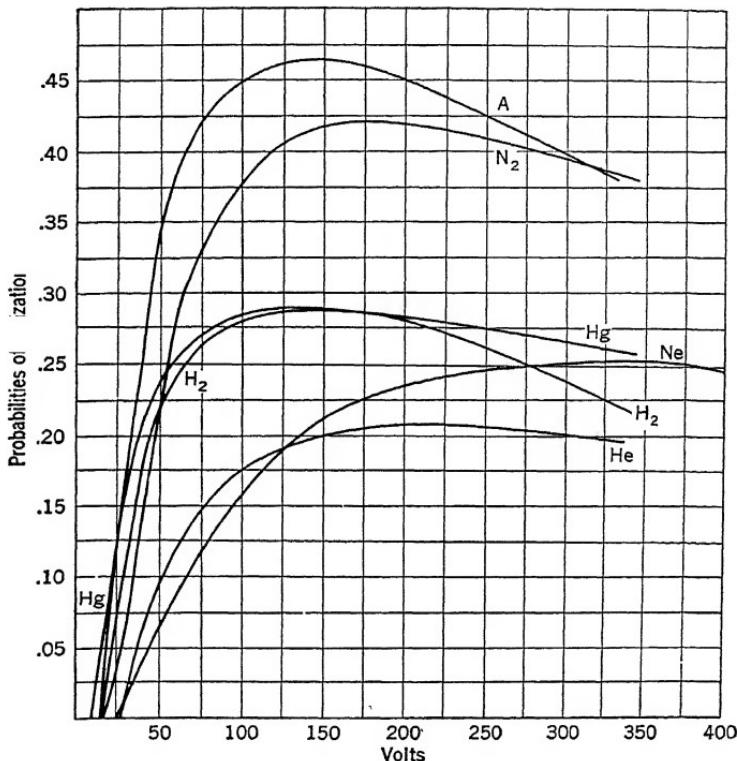


FIG. 10.—Probabilities of Ionization by Electron Impact as a Function of Velocity Expressed in Equivalent Volts, after Compton and Van Voorhis.

and awaits confirmation. In any case, it can be definitely stated that the probabilities of ionization and excitation, calculated on the basis of the electron free paths in a given gas, and the number of ions formed, are a maximum, possibly at, certainly not far above, the ionizing or exciting

potential; thereafter they drop more or less rapidly to lower values as the electron velocity increases. The order of magnitude of these probabilities is from values something like 0.5 to 0.001, depending on circumstances. Here, again, theory is quite incapable of dealing with the problem.

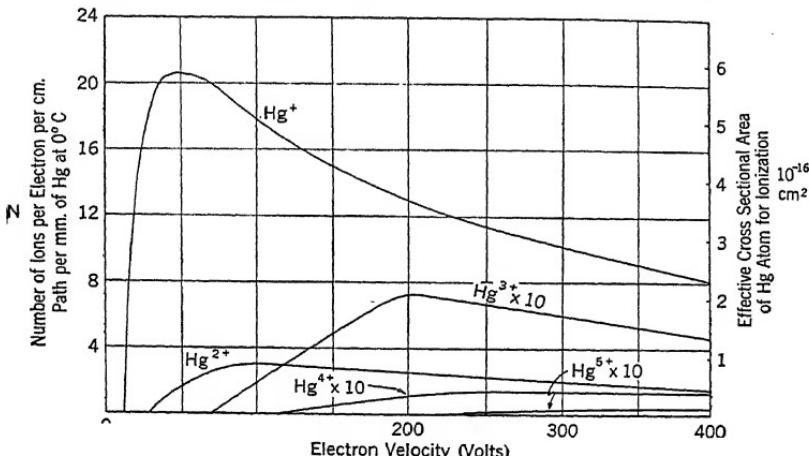


FIG. 11.—Bleakney's Curves for Single and Multiple Ionization of Mercury Atoms by Electron Impact as a Function of Electron Velocity in Equivalent Volts.

19. Ionization by Positive Ions and Temperature.—In what has gone before, some mention has been made of ionization by α particles, protons, positive atomic or molecular ions, and by neutral atoms of high energies. As regards the first two agents for high velocities (R 35), the mechanism is nearly described by the classical mechanics. For low velocities, where these agents are accompanied by electrons, as was stated, a new mechanism must be postulated (R 36). This mechanism is the same for the positive ions and for neutral atoms, the only advantage of the positive ions being that, owing to their charge, they can pick up energy from any electrical field present. The possibility of the ionization by positive ions is of great importance in the problem of electrical insulation, for the whole

mechanism of spark discharge and electrical breakdown of dielectrics depends on the ability of positive ions to ionize by impact, and on the conditions accompanying this ionization, as well as the efficiency of the process.

Numerous experiments have been made in analogy to the ionization potential experiments for electrons, using positive ions. In practically all cases, the results have been negative, or proven wrong when positive, for energies up to a few hundred volts (R 42; 14 Chapter 5). The difficulty in the problem is an experimental one due to the relatively great inefficiency of ionization by positive ions compared to electrons, and to the fact that positive ions and the conditions under which they are studied lead to many possible complications because of production of secondary electrons. For this reason, all results up to the recent measurements of Sutton (R 42) have been inconclusive or definitely negative. The latter has found that positive ions of Na or K, moving in gases such as He, Ne, Ar, N₂, and air, appeared to produce ions in these gases above 100 volts, the efficiency being the greater, the greater the atomic weight of the gas studied. In H₂, however, no effect of this sort was observed. While discredited by some, on account of possible disturbing effects from secondary electrons set free by such things as metastable atoms, the work appears on the whole reliable. Theoretical probabilities at higher energies appear to be too high, on the basis of other work, but may not be so. However, these calculations depend on assumptions as to free paths of positive ions, which do not enter into the direct interpretation of the measurements.

In any case, there are definite indications that positive ions can ionize by impact in a gas. Otherwise, it is impossible to account for the electrical discharge from a positively electrified point in a gas (R 43). A second argument comes from the fact that, as the gas pressure is increased from 0.1 mm of Hg to 10 mm of Hg in pure inert gases, the minimum sparking potential in those gases ceases

to be affected by the material of the metal cathode and becomes a function of the gas only (R 44).

Could it be proven that neutral molecules or atoms, given high enough energy, can ionize by impact, the case for ionization by positive ions would again be strengthened. Saha's theory (R 23) predicts the magnitude of ionization in heated gases, and the results obtained from light emission of various salts in flames as a function of the temperature bear out the theory (14 Chapter 5). Unfortunately, the conclusions are obscured by the fact that in flames and in electric furnaces, such as those of King (R 45), the chemical reactions present, or the thermionic emission of electrons, give free electrons in abundance. If the temperature is sufficiently high, these electrons in equilibrium may reach the average temperature of the gas and thus ionize efficiently. There is, however, one more bit of evidence in this case. It is experimentally known from the work of Rutherford (R 37) and Henderson that near the end of their range α particles gain one and even two electrons (becoming neutral helium atoms in the latter case). These particles, He^+ and He , are, however, able to lose these charges again in impact with neutral molecules, giving He^{++} or an α particle and He^+ . Since a helium atom can by impact with neutral molecules ionize itself, it must also be able to ionize the molecules of lower ionizing potentials.

Accordingly, it seems most probable that positive ions or neutral atoms with adequate energy can ionize on impact with neutral molecules or atoms, if they have the energy. The process has never been directly observed for positive ions of less than 100 volts energy. It is clear, however, from sparking data that this must occur at smaller energies, and Franck (14 Chapter 5), on theoretical considerations, places the value of the ionization threshold for positive ions at about 1.5 times the ionizing energy for electrons. The ionization probabilities even at 700 volts are still small compared to electrons, and it is likely that

at the minimum ionizing energy, given by Franck, the probabilities are of the order of 10^{-5} to 10^{-6} , as can be deduced from Sutton's work (R 45).

20. Conditions after Excitation or Ionization.—It is next of importance to consider what occurs after ionization or excitation has taken place (14 Chapter 6 gives a complete summary; see also 5 pp. 480, 496, 502). One might first regard the atom affected. In the case of excitation, certain facts have been quite definitely established. As a result of the studies of light emission by positive rays, after they enter a good vacuum, Dempster (R 46) and Wien (R 47) have shown that the atoms which have an electron in an excited state (i.e., in an outer orbit of higher quantum number), in general continue in that state for some 10^{-8} of a second, during which time light emission continues. Hence, the usual period of rest of an electron in an excited orbit, as well as the time taken to liberate the light in returning to the normal state, are both included in this time interval. Previous work on the length of paths over which light waves from a given source could interfere, indicated that, in the absence of frequent collisions, trains of waves were emitted over intervals of 10^{-8} seconds (R 46 and R 47 give good references). That is, the coherence of phase in an interferometer requires that the difference of path length, over which light waves from the same source can travel and yet interfere, gives a number of waves which are emitted in time intervals of the same *order of magnitude* as that comprising the *period of lingering in the excited state*, and the period of emission as shown by canal rays. Since experiments in arcs and discharges give evidence of one or more electron impacts on the atom while it is excited, the conclusion must be drawn that electrons remain in the excited orbits over finite intervals of time. This means that part of the interval $A \times 10^{-8}$ seconds over which light is emitted is spent in the outer orbit. How great a fraction of this time is so spent has not as yet been experimentally determined. Since the

wave trains indicate periods of the same length for the phenomena of emission, we can safely assert that the time in the excited state is of the order of 10^{-8} seconds, and that the act of emission also lasts about this long.

The actual process of light emission is, however, unknown. How the electron is accelerated in going from one orbit to another (if at all), and how this causes radiation, can hardly be conjectured to date, but can be expressed in the equations of wave mechanics.

There are cases, however, where the electron is placed in an outer orbit of higher energy from which it cannot readily get back to the initial state. Such a state is called a *metastable* state (5 p. 502 ff.; 14 pp. 6 and 232), and in this case the electron may remain in a higher energy orbit for very much longer time intervals, such as 10^{-4} or less seconds (see 14 p. 232 for references). These metastable states may differ from some one of the ordinary excited states by very small energy differences. Accordingly, frequently by a small increment or decrement of energy, such electrons in metastable states can be thrown back to the normal excited orbits whence they radiate light in the usual 10^{-8} seconds. Such changes are produced quite readily by impact of the metastable atoms with certain particularly active molecules (R 48). Many of the monatomic gases possess metastable states, notably neon, helium, argon, mercury, as do probably some of the molecules. These states are of great importance in many discharge tube and other phenomena, as they give time for the atoms to diffuse or collide with appropriate atoms and molecules, and thus to transfer their energy to these in collision (see 5 p. 502 ff.; 14 p. 238, for references).

21. Inelastic Impacts of the Second Class.—It was through the existence of such states that Franck was able to prove the existence of the new type of impacts called "inelastic impacts of the second class" (14 p. 210 ff.; 5 Chapter 16). These impacts were first theoretically predicted by Klein and Rosseland (R 22) as a result of ther-

modynamical reasoning. These men considered an ionized gas at high temperatures in thermal equilibrium. In such an equilibrium, it is clear that if an electron can approach a neutral atom and ionize it, giving rise to a second free electron and a positive atom ion, the first electron having lost energy, the reverse process must also occur with equal frequency (*principle of detailed balancing*). In the reverse process, two electrons of low velocity approaching an ionized atom, or atom ion, must be able to interchange velocities, so that while one electron neutralizes the atom, the other electron escapes with the total energy resulting from the process. Such an impact is called an inelastic impact of the second class. Another example would be one in which a free slow electron approached an excited atom and the energy of excitation was given the slow electron while the excited electron returned to its normal orbit *without radiation*, or to some intermediate orbit with radiation of lower frequency. This is the inverse of an exciting impact. Under ordinary conditions, the gas is far from temperature equilibrium, and electrons and excited atoms are few; hence the phenomena described are rarely observed. In certain discharge tube phenomena, Langmuir (R 49) and Franck (14 p. 214) believe to have found evidence for this action at high electron concentrations. The effect is however probably due to electrical oscillations in the discharge (R 51). Recent more direct evidence for such phenomena have been obtained by Leipunsky and Strauff (R 50), using high electron densities in phosphorus vapor excited by oxidation. In the case of the metastable states, the long life of these atoms in the active state enables such events to occur sufficiently frequently to be observed. The transitions most frequently observed, however, are not the passing of the excitation energy to free electrons, but rather to electrons in other atoms. Thus Hg vapor irradiated by light from the line 2537 Å from a quartz mercury arc becomes activated (i.e., enters the metastable state). If these atoms collide with thallium atoms while in this state,

a thallium electron is raised to a higher level, so that it emits the green thallium line, and the difference between the energy of the line, 2537 \AA , and the low energy thallium line is converted into kinetic energy of the separating Hg and Tl atoms after impact (see 14, p. 227 for references). If the Hg strikes H_2 or hydrocarbon vapor molecules in the excited state, the energy is converted into the work of dissociation of these molecules, into atoms of H_2 (R 52) or fragments of the hydrocarbon (5 p. 507 ff.). Finally, if the excited atoms collide with atoms of lower ionizing energy, these may remove an electron of the neutral atom, ionizing it and returning the Hg atom to the normal state. Such impacts are all termed by Franck inelastic impacts of the second class. The chances of such energy transfers are not always very high. They are, however, much higher, the more nearly equal the energy of the excited atom is to the energy required by the atom or molecule struck in order to produce the effect observed. Since these effects occur for metastable atoms, no matter how produced, and as these are readily produced in some gases, it is clear that they can play an important rôle in many discharge phenomena. The metastable atoms are of vital importance in the production of photochemical reactions, and can also react with metal surfaces to give electrons.

Akin to the reactions produced by metastable atoms with other atoms or molecules, we have the phenomena produced by atoms or molecules in the ionized state. Evidence is at hand, both theoretical and experimental, that at low temperatures (far below equilibrium for ionization) the electron and the atom ions, or ionized molecules, show great reluctance at recombining (5 p. 467 ff.; R 53). This is, in general, conditioned by the fact that in order to recombine with a positive atom, the electron is accelerated in the field of the ion, and unless it can radiate the excess energy, it will escape from the ion without recombining. Now the chance of such radiation by a returning

electron appears to be relatively small. If it did radiate in the process of capture, the wave length radiated would be determined by the relation that the energy of the electron $(1/2)mv^2 = h\nu$. Since electrons exist in the gas with all sorts of initial energies, the returning electrons would radiate all possible frequencies beyond ν_0 , that which constitutes the outermost orbit or state before ionization occurs. Hence the recombination spectrum of electrons and atom ions, or of electrons and charged molecules, is a continuous spectrum (5 p. 469 ff.; 14 p. 98 and 183). These continuous spectra are always observed at the end of the series spectrum of some atoms. The intensity is at best weak, but is stronger the nearer the frequency of the light radiated is to the end of the series spectrum. This is to be expected from the rule cited for metastable atoms, namely, that the transitions are the more probable the less energy there is to get rid of. Hence, in the absence of a large concentration of free low-velocity electrons, the positively charged portions of the atoms or molecules remain charged for considerable periods of time. In this respect, they behave somewhat like metastable atoms (5 p. 506 ff.). In fact, the reluctance of positive ions to recombine with electrons is shown by the fact that the electrons probably attach more readily to neutral molecules (where the energy gained from attractive forces, and hence required to be dissipated, is less) than they do to positively charged particles (R 53). The positive ions, and the negative ions formed by combinations of electrons and molecules, then recombine quite readily, for in this case opportunities for energy dissipation in the impact of the molecular ions are greater. Of course, were enough free electrons present in a gas to give the three-body impact (triple impact) of two electrons and a positive ion (which characterize inelastic impacts of the second class), the recombination of positive ions with electrons would be facilitated. Under ordinary conditions in gases, this occurrence is most rare.

The long-lived positive ions in their rôle as pseudo-metastable atoms can, however, do other things. They can remove electrons from atoms of lower ionizing energy or from metal walls of a vessel, either exchanging charges or liberating free electrons. In the case of the exchange of charge between a positive ion and neutral molecules or atoms, it becomes sometimes impossible to know the nature of the charged carriers in gases, even though molecules of one sort in the gas were initially ionized (R 53). The same consideration holds for doubly and multiply charged ions, and is the reason for the observed fact that, while it is known that multiply charged atoms or molecules are created by single electron impact, such carriers cannot be detected in a gas, after any considerable time interval (for example, 10^{-2} seconds). Again, the more nearly equal the ionizing potentials of the positive ion and the colliding molecule are, the more likely the change in charge. The difference in energy is then either converted to kinetic energy of separation, to radiation, or to excitation of the atoms or molecules concerned.

22. Dissociation of Molecules by Electron Impact.—As was stated in the introduction, the atoms in a molecule are held together by either the formation of pairs or octettes of electrons in which the latter more or less surround the two nuclei. Since an electron of high enough energy is still very light, it seems obvious, according to the laws of momentum and energy, that on impact, this electron can hardly impart to the massive nuclei the energy necessary to dissociate the molecule. However, positive-ray studies with the mass spectrograph, as well as chemical reactions produced by electron impact and spectroscopic studies, indicated ready dissociation of molecules on single ionization by electron impact. At first, the naive idea that one or both of the paired electrons (or some essential cementing electron in the structure) had to be removed for dissociation was suggested. Later certain quantitative behavior of dissociation products of molecules, as a function of gas

pressure, was assumed to indicate that after ionization or activation an impact with a neutral molecule was needed to produce dissociation (5 p. 461; 14 Chapter 7; R 31). These experiments have recently been called into question, however, and it is doubtful whether this mechanism plays any important part at all.

The solution for dissociation by electron impact was suggested by Franck in 1926 (5 p. 395 ff.; 14 p. 275 ff.), and later worked out by Condon (5 pp. 392 to 403), both on quantum and wave mechanics. Franck recalled the fact that, at normal temperatures, a great many molecules have the less tightly bound atoms set into vibrational motion. Since the period of vibration is slow, compared to that of electron ejection by an electron impact or by light, or slow even compared to the time of an electron transition in an atom, such a change can occur at any point in a vibrational cycle. At certain phases of the vibration, the distance between the nuclei may be considerable. Since the energy distribution in the molecule is a function of the condition of all its electrons, one can see that the energy distribution and the potential function of the nuclei (which depends on the distance between them) will be radically affected by such factors as the loss of an electron or its removal to an outer orbit. If now an electron be removed or excited at the right value of the distance between nuclei in a vibration, so that the energy distribution following emission at this distance would indicate the probability of dissociation, the two nuclei will separate. It must, of course, be understood that this can occur only when the energy given by the disturbance of the electron, plus the energy which can be obtained from the vibrational state, exceeds the energy of dissociation. This mechanism has been verified accurately by Condon for a large number of spectra in relation to the intensities of various bands, and is doubtless correct. Thus any occurrence leading to ionization of a molecule or excitation, such as electron impact, light absorption, or impact with a

metastable or excited atom or molecule, can, when enough energy is involved, lead to dissociation, and hence to chemical reactions. Actions of this nature play an important rôle wherever ionization, especially in liquids and gases, is called into play.

It is thus seen that the normal excited state of an atom lasts perhaps some 10^{-8} seconds, followed by radiation consuming a time interval of the same order of magnitude. In so far as further reactions of the excited atoms are concerned, such actions are of importance only under conditions where high electron densities exist, in view of the short time intervals involved. Some atoms can, however, have electrons in metastable states of excitation lasting some 10^{-4} seconds. Here, even at lower electron densities, second impacts can change the phenomenon, and such atoms in impact with neutral atoms or molecules of an appropriate sort can lose energy by inelastic impacts of the second class, causing excitation, ionization, or dissociation of molecules. Owing to the difficulty of electron energy dissipation in the field of positive ions, the electrons cannot combine with these ions readily. When they do recombine, the various speeds of recombining electrons cause the emission of continuous spectra just beyond the series limit for the given series. Positive ions, and especially positive ions of higher energy, such as multiply charged ions, have a long life in a gas, so that, like the metastable atoms, they can transfer their energy to other molecules, and even steal electrons from them. In general, changes of this sort are the more probable the nearer the energies of the possible changes are together, for the losses to radiation or to kinetic energy of atoms in processes of exchange are rather unlikely. These conclusions lead to a fairly clear picture of the life of positive ions in a gas. The long life enables them to encounter many molecules, and to end up eventually as neutral molecules by picking electrons from metal surfaces or electrodes, if they have not picked them up elsewhere.

In the case of free electrons, liberated in the process, it was seen that they occasionally united with positive ions, emitting light. Usually, however, if the right molecules are present (for example, O₂, Cl₂, etc.) (R 54), they will unite with neutral molecules to form negative ions. These can recombine more readily with positive ions than electrons, and neutralization can occur by this process. Finally, if the electrons cannot form ions (R 54), they diffuse or are swept to the electrodes or walls of the vessel by space charges or fields, and there are neutralized.

23. Photoelectric Processes Leading to Ionization in Gases.—Since electron bombardment of gas molecules and atoms can lead to an activated state and subsequent radiation of light, it is not unreasonable to suppose that light radiations can in turn cause a liberation of electrons from atoms and molecules (5 p. 467 ff.). The effect was first discovered in the case of the reaction of ultra-violet light on polished metal surfaces, and later by the liberation of electrons of higher energy from all substances by X-rays. More recently, Williamson (R 55), and then with more certainty Mohler and Lawrence (see 5, p. 468 for references), proved the ionization of atoms of gases by ultra-violet light, though the same effect caused by X-rays in gases had long been known.

These processes are all governed by the well-known Einstein (4 p. 162 ff.; 7 p. 236) photoelectric equation:

$$(1/2)mv^2 = h\nu - h\nu_0 \quad (78)$$

where $(1/2)mv^2$ is the kinetic energy of the electrons liberated, ν is the frequency of the radiation absorbed (X-rays or light waves), and ν_0 is the frequency which will just remove an electron from the surface of the atom. Here, again, h is the Planck constant, and $h\nu_0$ represents the work necessary to pull an electron out of the surface of the metal or the atom considered. In the case of a metal, the electrons are supposed to be free in the metal, and the work $h\nu_0$ is the work to remove an electron from the sur-

face. It is closely related to the work necessary to remove an electron from a metal filament by temperature, and is characteristic of the metal. In a gas atom or molecule, $h\nu_0$ is the work required to remove the electron acted on from its normal orbit to the limiting orbit of the series i.e., it is simply the ionization potential of the particular electron in question. Hence, below a frequency ν_0 , we can, in no case, remove an electron by light. This frequency is known as the *photoelectric threshold*. When a gas is ionized by electron impact, the electron must first of all have enough energy to ionize. Next, the chance that the electron will cause ionization of the atom must be considered; i.e., in analogy one may ask what the chance is that the light will react with the atom in such a manner as to cause ionization. In the case of the photoelectric effect in a gas, not only must the incoming light have a frequency ν greater than ν_0 , but the light to be effective must be *absorbed* by the atom. If the light has a frequency ν , near ν_0 but greater than that value, the probability of absorption is greatest. Beyond this, the probability is small, and when we regard the extreme case of hard X-rays and H₂ molecules, where the frequencies are quite discordant, ionization is very rare.* In general, photoelectric ionization in gases is a rare phenomenon because of the low absorption coefficients for higher energies. It is this low efficiency, coupled with the strong photoelectric effects due to metal parts of the apparatus (metals, because of free electrons, absorb energy very readily), that made detection of the true photoelectric effect in gases very difficult. Photoelectric ionization of gases must be taken into account, however, in various problems involved in the processes of ionization in gases. While the *energy of the emergent electrons* depends on the

* It is because of the rare ionization of light atoms or molecules by X-rays and the high energy of electrons liberated by the X-rays that considerably more than 99 per cent of the ions formed in gases under the influence of X-rays are of secondary origin produced by the rapidly moving photo electron in its passage through the gas.

frequency of the incident light, the *intensity of the effect*, i.e., the *number of electrons liberated per second*, depends on the *intensity* of the light.

An effect of the same nature, but of much greater frequency and importance, is the activation of a molecule or an atom by an appropriate frequency ν of radiation. If one atom, A , has an electron which can be raised to a certain state α by an energy $h\nu_\alpha$, then if a radiation of frequency greater than ν_α falls on this atom A , the electron might be raised to its higher state and an excited atom produced.

This process cannot occur when the two frequencies are quite different from each other, since there is no mechanism by which the energy difference $h\nu - h\nu_\alpha$ can be dissipated. If, however, the value of ν is just about equal to ν_α , the light is very readily absorbed. Since, in any light source, the frequencies ν_α are somewhat spread due to the Doppler effect originating from translational and rotational motion of the molecules, the values of ν_α obtained from a single transition in the source are sufficiently varied so that similar atoms in the absorbing gas can readily absorb the radiation. The atoms activated in this fashion, by light of the same frequency from another source, continue excited some 10^{-8} seconds, if normal, or some 10^{-4} seconds or more if metastable, and then re-radiate their energy in all directions. Such radiation is called *fluorescent radiation* (25 Chapters 1 and 2). Thus, for normal atoms, fluorescent radiation may be radiated and absorbed and radiated and absorbed many times by atoms of a gas before being lost to the gas (R 56). This temporarily "imprisoned" radiation and its activated atoms can, of course, produce results on impact with other atoms or molecules similar to atoms activated in other ways. The fluorescent radiation, especially if metastable states are excited, can cause dissociation and chemical reactions. Franck and Cario used light from the quartz mercury arc and let it activate atoms of Hg mixed with H₂. In this manner, they

were able to show the dissociation of H_2 by activated Hg atoms in the absence of the complications attendant on electron bombardment (5 p. 507 ff.).

Finally one phenomenon of somewhat rare occurrence in connection with photoionization should be mentioned, since it leads to the formation of multiple ions. It was demonstrated by Auger (R 57) for X-rays. If an X-ray liberates an inner electron from a *K* ring in an argon atom, the electron from the *L* shell may fall to the *K* level, emitting a characteristic *K* series X-ray. This X-ray in escaping from the atom is highly absorbed in that atom (20 per cent or more being the probability), and can give rise to an electron of high energy being liberated from an outside shell of the atom. The empty space in the *L* shell can then be taken up by an *M* electron liberating a characteristic *L* X-ray. This X-ray, in turn, may tear an electron from the outermost electron level in the atom, and so on. In this way, because the initial *K* electron was ejected with high energy, a second electron from the outside with lower energy and a third electron from the outside with a still lower energy are ejected from a single atom by an initial X-ray pulse. While the phenomenon is rare, it can occur, and should be taken account of, for it leads to multiply charged ions by a photoelectric process.

In general, then, we must note that molecules or atoms of a gas can be ionized or excited, and that molecules can be dissociated by absorption of light or X-rays. Except for excitation of atoms and molecules by light of just the right wavelength, the phenomenon is not frequent or efficient. It is very important, however, in photochemical reactions.

Before closing the discussion, a few words must be said about the importance of the walls of a container of gas, especially metal walls and electrodes, in the studies of the conductivity of gases and ionization in general. Beyond the effect of walls as recipients for ions by diffusion, etc., producing field disturbances, and giving opportunity for

recombination and redistribution of charges, metal walls are especially important as they give rise to electrons by photoelectric processes, due to light or X-rays (4 Chapter 6). These conditions lead to the presence of electrons in the gas in large numbers, because of the relatively large numbers of photoelectrons * liberated by metals; this fact may play a very important rôle in electrical breakdown. Furthermore, the electrons liberated from the walls produce conditions where there are more electrons in the gas, and hence more negative electricity than there is positive; many early measurements on discharge through gases were worthless because of neglect of this difficulty. Again, the walls, but especially metal walls and electrodes, become adequate sources of electrons on bombardment by positive ions (R 58), by electrons, and probably even by activated or metastable atoms (R 59). If a metal surface is carefully outgassed by bombardment with electrons and heating, the positive ions can knock out but few electrons, 1 electron per 1000 positive ions at 1000 volts or so of energy (R 60). If, however, gas films of certain sorts are present, 20 volt positive ions can liberate electrons at much higher rates, 1 electron to 100 ions. The alkali metals, and in general metals with low photoelectric threshold, are particularly susceptible to electron emission, be it by light, metastable atoms, or positive ions. The kinetic energy of the positive ions plays an important part in such processes, although theoretically both positive ions and metastable atoms of sufficiently high energy should liberate electrons from surfaces irrespective of velocities.

24. Sources of Ionization in Gases.—In conclusion, as a summary to the discussion of the behavior of atoms and molecules and the nature of the external electronic disturbances found, one might name the actual sources of ioniza-

* Since metals, on account of free electrons, can absorb all frequencies of light not reflected, and since absorption is confined to very thin layers at the surfaces, the number of electrons liberated photoelectrically in metals is thousands of times greater than the number liberated from atoms in a gas by light.

tion observed in gases. They are as follows, and require little explanation on the basis of what has gone before:

- I. Processes in the gas itself.
 1. Rapidly moving electrons, including β rays from radioactive changes.
 2. Rapidly moving positive charges, protons, and α particles.
 3. Rapidly moving positive ions in high fields.
 4. Photoelectric ionization by ultra-violet light, X-rays, and γ rays.
 5. Through chemical reactions in the gas, e.g., oxidation of NO to NO_2 , or of P vapor to P_2O_3 , or P_2O_5 .
 6. Possibly ionization of the gas may be caused by temperature alone without action of the walls, or by impact of rapidly moving neutral atoms or molecules from other sources (e.g., neutralized α rays).
- II. Processes due to solid or liquid surfaces in contact with the gas.
 1. Bombardment of metal by fast electrons, α particles, positive ions, or recoil atoms, giving secondary electrons.
 2. Action of metastable atoms on solid surfaces, giving secondary electrons.
 3. Action of γ rays, X-rays, and light on solid or liquid surfaces, giving electrons, photoelectric effect.
 4. Incandescent metals in general emitting large numbers of electrons, called thermionic emission.
 5. Incandescent surfaces having salts, phosphates, oxides, chlorides, or complex metal surfaces of mixed composition at lower temperatures give positive ions such as Na^+ , K^+ , Ba^{++} , etc.
 6. Chemical reactions at surfaces, oxidation of moist P, or Na and K, give ions of both signs, but more negative ions.
 7. The atomizing of liquids into minute droplets by high-velocity air currents tangential to the surface causes the smallest droplets to become negatively charged. If water is used which contains ions, the larger droplets have ions in them and are predominately positive. This source of conductivity of the gas is the source of the charges on rain clouds and thunder showers.
 8. Frictional effects between solid particles suspended in gases, as typified by electrification in sandstorms.

APPENDIX I

RADII OF MOLECULES DETERMINED BY VARIOUS METHODS

Radii are all given in 10^{-8} cm.

Method	Cl ₂	Br ₂	I ₂	(CN) ₂	HF	HCl	HBr	CO	CO ₂	H ₂ O
From $b = RT_k/8p_k$, (Van der Waals)	1.654	1.893	1.590	2.276	1.614	1.443	
From $b = RT_k/15p_k$ (Wohl).	1.341	1.545	1.290	1.844	1.309	1.170	
Tetrahedral packing in liquids	3.68	3.90	2.84	3.31	3.52	3.37	3.65	2.74	
	$T = -80^\circ$	$T = -4^\circ$		$T = +13^\circ$	$T = -83^\circ$	$T = -65^\circ$	$T = -205^\circ$	$T = -34^\circ$		$T = +4^\circ$
Gas isotherms.....
Slow-moving electrons.....	1.85	2.02	2.23	2.04	1.83
Viscosity.....	1.647	1.859	1.368	1.517	1.36
Molecular refraction.....	0.92	1.130
Diamagnetism.....
Molecular distance from:										
Band spectra.....	1.34	1.49	1.14
Chemical constants.....	{ 0.924	1.276	1.419	0.94
Dipolar distance.....	0.025	0.0075	0.2

IONIZATION PHENOMENA

APPENDIX I.—(Continued)
RADII OF MOLECULES DETERMINED BY VARIOUS METHODS

Radii are all given in 10^{-8} cm.

Method	He	Ne	Ar	Kr	X	Hg	H ₂	N ₂	O ₂
From $\delta = RT_k/8p_k$ (Van der Waals)	1.15 1.321 1.437	1.43 1.437	1.57	1.71	1.186	1.380	1.573	1.453
From $\delta = RT_k/15p_k$ (Wohl)	1.071	1.165	1.27	1.39	0.962	1.119	1.276	1.178
Tetrahedral packing in liquids	3.17 $T = -271.5^\circ$ $T = -189^\circ$	3.20 $T = -146^\circ$	3.55 $T = -102^\circ$	3.51 $T = -39^\circ$	2.58 $T = -258^\circ$	3.15 $T = -202^\circ$	3.35 $T = -227^\circ$	3.08
Gas isotherms..... $T = 0^\circ$	1.39	1.16	1.49	1.325
	1.12 $T = 293^\circ$ 1.275	1.21 2.77	2.04	1.75	
	1.41 $T = 0^\circ$ 1.275	2.77	1.78			
Slow-moving electrons.....	1.17 0.922	1.43 1.48	1.59 1.666	1.75 2.002	1.82	1.088	1.58	1.48	
Viscosity.....	0.741	0.55	0.929	1.20	1.169	
Molecular refraction.....	1.46	0.76	0.65	
Diamagnetism.....	2 × 0.25	2 × 0.56	
Molecular distance from: Band spectra.....	2 × 0.26	2 × 0.77	2 × 0.77	
Chemical constants.....	2 × 0.18	2 × 0.97	2 × 1.35	

APPENDIX II
MOLECULAR VELOCITIES, MEAN FREE PATHS, AND DIAMETERS

Gas	Velocity at 0° C., cm./sec.	Mean Free Path, <i>L</i> , cm.	Molecular Diameter from	
			Viscosity η , cm.	Vander Waals, cm.
Hydrogen, H ₂	18.39×10^4	18.3×10^{-6}	2.47×10^{-8}	2.32×10^{-8}
Helium, He.....	13.11×10^4	28.5×10^{-6}	2.18×10^{-8}	2.30×10^{-8}
Nitrogen, N ₂	4.93×10^4	9.44×10^{-6}	3.50×10^{-8}	3.53×10^{-8}
Oxygen, O ₂	4.61×10^4	9.95×10^{-6}	3.39×10^{-8}	
Neon, Ne.....	5.61×10^4	19.3×10^{-6}		
Argon, A.....	4.13×10^4	10.0×10^{-6}	3.36×10^{-8}	2.86×10^{-8}
Krypton, Kr.....	2.86×10^4	9.49×10^{-6}		3.14×10^{-8}
Xenon, Xe.....	2.28×10^4	5.61×10^{-6}		3.42×10^{-8}
Chlorine, Cl ₂	3.07×10^4	4.57×10^{-6}	4.96×10^{-8}	
Methane, CH ₄	6.48×10^4	7.79×10^{-6}		
Ethylene, C ₂ H ₄	4.88×10^4	5.47×10^{-6}	4.55×10^{-8}	4.68×10^{-8}
Carbon Monoxide, CO..	4.93×10^4	9.27×10^{-6}	3.50×10^{-8}	
Carbon Dioxide, CO ₂ ...	3.92×10^4	6.29×10^{-6}	4.18×10^{-8}	3.40×10^{-8}
Ammonia, NH ₃	6.28×10^4	6.95×10^{-6}		
Nitrous oxide, N ₂ O.....	3.92×10^4	6.10×10^{-6}	4.27×10^{-8}	
Nitric oxide, NO.....	4.76×10^4	9.06×10^{-6}	3.40×10^{-8}	
Sulph. Hydrogen, H ₂ S...	4.44×10^4	5.90×10^{-6}		
Sulph. dioxide, SO ₂	3.22×10^4	4.57×10^{-6}		
Hydrochloric acid, HCl..	4.30×10^4	6.86×10^{-6}		
Water, H ₂ O.....	7.08×10^4	7.22×10^{-6}	4.09×10^{-8}	

APPENDIX III

For convenience in conversion of electron energies into volts, to kinetic energies in ergs, to degrees absolute in equilibrium, to frequencies of emitted radiation, and to wavelengths of light, the following factors and relations are given:

$$Ve = (1/2)mv^2 = (3/2)kT = h\nu = hc/\lambda$$

V = Potential in absolute e.s.u.

V_v = Potential in volts $V/300$

m = Mass of electron = $(8.99 \pm 0.014) \times 10^{-28}$ grams

v = Velocity of the electron in cm./sec.

k = Boltzmann gas constant = $R_0/N_0 = (1.3708 \pm 0.0014) \times 10^{-16}$ ergs/deg.

e = Charge on the electron = $(4.77 \pm 0.005) \times 10^{-10}$ abs e.s.u.

h = Planck constant of quantum action = $(6.547 \pm 0.008) \times 10^{-27}$ ergs sec.

T = Temperature in degrees Kelvin = $273.18 \pm 0.03^\circ$ K = 0° C.

ν = Frequency of emitted light in cycles per sec.

λ = Wavelength of light in cm.

c = Velocity of light = $(2.99796 \pm 0.00004) \times 10^{10}$ cm/sec.

Hence

$$\begin{aligned} V_v &= (300/e)(1/2)mv^2 = (3/2)kT(300/e) = h\nu(300/e) \\ &= (hc/\lambda)(300/e) \end{aligned}$$

Whence to slide rule accuracy, we have the following values of the conversion factors for quick computation:

$$\text{Kinetic energy in ergs} = \frac{4.77 \times 10^{-10}}{300} V_v \quad 1.590 \times 10^{-12} V_v$$

$$T^\circ \text{ in degrees absolute} = (2/3) \frac{4.77 \times 10^{-10} V_v}{300 \times 1.371 \times 10^{-16}} \quad 7730 V_v$$

$$\nu \text{ in cycles per sec.} \quad \frac{4.77 \times 10^{-10} \times V_v}{300 \times 6.547 \times 10^{-27}} \quad 2.428 \times 10^{14} V_v$$

$$\lambda \text{ in cm.} \quad \frac{6.547 \times 10^{-27} \times 300 \times 2.9979 \times 10^{10}}{4.77 \times 10^{-10} V_v}$$

$$\frac{1.235 \times 10^{-4}}{V_v}$$

Other useful constants are:

Volume of a perfect gas (0° C.,

$$A_{45}) \quad R :: (22.4146 \pm 0.0008 \text{ liters/mol.}$$

Atmosphere at Lat. 45°, $A_{45} :: (1.013199 \pm 0.000003) \times 10^6 \text{ dyne/cm}^2.$

Mechanical equivalent of heat

$$J_{15} :: 4.1852 \pm 0.0006 \text{ abs. Joule/Cal}_{15}.$$

Faraday constant

$$F :: 96489 \pm 7 \text{ abs. Coul./g. equiv.}$$

Avogadro's number

$$N_A = (6.046 \pm 0.006) \times 10^{23} \text{ per mol.}$$

Number of atoms/cm.³

$$\text{Loschmidt number} \quad N :: (2.70560 \pm 0.003) \times 10^{10} \text{ per cm}^3.$$

Gas constant per mol

$$R_o = (8.3136 \pm 0.001) \times 10^7 \text{ ergs/deg. mol}$$

$$:: (1.9864 \pm 0.0004) \text{ Cal}_{15}/\text{deg. mol.}$$

Mass of atom of unit atomic

$$\text{weight} \quad :: (1.6489_8 \pm 0.0016) \times 10^{-24} \text{ g.}$$

Potential associated with unit
frequency

$$= (1.3725_4 \pm 0.0005) \times 10^{-17} \text{ ergs sec. per e.s.u.}$$

Frequency associated with unit
potential

$$= (7.2857_7 \pm 0.0027) \times 10^{16} \text{ e.s.u./erg sec.}$$

$$(2.4302_5 \pm 0.0009) \times 10^{14} \text{ per sec. abs. volt.}$$

Wavelength associated with ab-
solute volt

$$= (12336.1 \pm 5) \times 10^{-8} \text{ cm. abs. volt.}$$

Energy of 1 absolute volt elec-
tron

$$= (1.5910_8 \pm 0.0016) \times 10^{-12} \text{ ergs.}$$

Speed of 1 absolute volt electron = $(5.9481_1 \pm 0.0034) \times 10^7 \text{ cm./sec.}$

See also Tables of Physical Constants printed at the beginning of various volumes of *Handbuch der Physik*, edited by Geiger and Scheel (Springer), or Birge, R.T., *Phys. Review Supplement*, Vol. 1, pp 1-73, 1929.

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INDEX OF NAMES

- ANDERSON, J. A., 12, 135
ANDRADE, 134
ASTON, 134
AUGER, 126, 136
AVOGADRO, 1, 57, 58, 62, 70, 133

BAERWALD, 135, 136
BALMER, 24
BARKLA, C. G., 34
BARUS, 96
BENADE, J. M., 101, 135
BENNETT, R. D., 135
BERNOULLI, 2, 83
BIRGE, 133, 134, 135
BLEAKNEY, 104, 110, 136
BLOCH, 134
BOHR, 19, 20, 22, 25, 31, 98, 102, 103,
 108, 136
BOLTZMANN, 59, 75, 77, 78, 85, 95, 132
BONNHOFFER, 45
BRACKETT, 25
BRAGG, W. H., 134
BRAGG, W. L., 134
BRIDGMAN, 134
BROWN, 99

CARIO, 125, 136
CLAUSIUS, 2, 63, 64
COMPTON, A. H., 134
COMPTON, K. T., 101, 110, 111, 135
 136
CONDON, 121, 134, 136
CORNISH, 87
COULOMB, 6, 10, 18
CROWTHER, 134

DALTON, 1, 2, 57
DARROW, K. K., 134
DAVISSON, 4, 135

DEBYE, 88, 134
DEMBER, H., 135
DEMPSTER, 104, 115, 136
DOPPLER, 42, 44, 125
DULONG, 2, 83, 84
DUMAS, 2

EASTMAN, 87
ECKART, 135
EINSTEIN, 84, 88, 123
EUCKEN, 87

FARADAY, 58, 133
FLETCHER, 97
FOOTE, 134, 136
FOWLER, 25, 136
FRANCK, 99, 104, 114, 115, 116, 117,
 121, 125, 134, 135, 136
FRANKLIN, 4
FUCHS, 134

GAY-LUSSAC, 1, 2, 57
GERLACH, 134
GERMER, 4, 78, 135
GIAUQUE, 135
GOUDSMIT, 135

HANLE, 136
HARRIES, 100, 135
HELMHOLTZ, 2
HENDERSON, 114
HERTZ, 99, 135, 136
HERTZFIELD, 135
HOGNESS, 104, 136
HOLST, 31
HOUSTON, 135
HUGHES, 135

JACKSON, 136

137

- JOFFÉ, 134
- JOHNSTON, J. A., 135
- JORDAN, P., 134
- JOULE, 2, 59, 61, 62, 63, 70
- KALLMANN, 104, 136
- KELVIN, 2
- KING, A. S., 114, 135, 136
- KLEIN, 89, 116, 135
- KNIPPING, 136
- KOSSEL, W., 26
- KRAMERS, 31
- LANGMUIR, 117, 136
- LAURITSEN, C. C., 135
- LAVOISIER, 1, 2
- LAWRENCE, 111, 123, 136
- LEIPUNSKY, 117, 136
- LEWIS, G. N., 26, 28, 134
- LINDEMANN, 84, 88
- LOEB, 134, 136
- LOSCHMIDT, 57, 58, 67, 133
- LUNN, 136
- LYMAN, 24
- MARSHALL, 136
- MAXWELL, J. C., 19, 66, 72, 77, 78, 85, 93, 95
- MAXWELL, L. R., 104, 136
- MAYER, 2
- MEGgers, 135
- MENDELEJEFF, 11
- MILLIKAN, 12, 14, 58, 97, 134
- MOHLER, 123, 134, 135
- MORSE, 134
- MOSELEY, 11, 34
- NERNST 84, 88
- NEUMAN, 136
- NEWTON, 99, 106, 109
- OLIPHANT, 136
- PAULING, 135
- PERRIN, J., 2, 58, 135
- PETIT, 2, 83, 84
- PICKERING, 25
- PLANCK, 7, 59, 84, 123, 132
- PRINGSHEIM, 135
- RICHARDSON, 135
- RICHTMYER, 1, 134
- ROSEN, 136
- ROSSELAND, 89, 116, 135
- RUARK, 134
- RUSSELL, 136
- RUTHERFORD, 6, 10, 11, 12, 58, 114, 135, 136
- RYDBERG, 24
- SAHA, 90, 114, 135
- SAUNDERS, 136
- SMYTH, H. D., 104, 136
- SOMMERFELD, 25, 134, 135
- STERN, O., 4, 135
- STRAUFF, 117, 136
- SUTTON, 113, 115, 136
- TAIT, 66, 71
- THOMSON, G. P., 4, 135
- THOMSON, J. J., 15, 134
- THOMSON, W., 70
- TONKS, 136
- VAN DER WAALS, 70, 129, 130, 131
- VAN VOORHIS, 110, 111, 136
- WAHLIN, 136
- WEBB, H. W., 136
- WIEN, 115, 136
- WILLIAMSON, 123, 136
- WOHL, 129, 130
- WOOD, R. W., 135

SUBJECT INDEX

A

Absorption of X-rays in atoms, internal, 126
Absorption spectra, infra-red, 87
Absorption in surfaces, 55
Accelerated charge, radiation of energy by, 19
Alcohols, structure of, 52
Alkalis, structure of, 52
Alpha particle, constitution of, 14
Alpha particles, 9, 10, 12, 13, 14, 58, 91, 107, 108, 112, 114, 128
change of charge of, 108, 114
charge on, 58
in nucleus, 12
ionization by, 107, 112
scattering of by nuclei, 10
velocity of, 12
Alpha prime groupings in nucleus, 14
Alpha ray, change of atomic number by, 13
Ammonia, structure of, 29, 53
Analogies, danger of mechanical, 3, 99, 109
Argon atom, structure of, 31
Artificial disintegration, 9, 13, 98
Association, molecular, 53, 95, 96
Atmospheric pressure, 133
Atom, excited and metastable, 43, 53, 86, 115, 118, 119, 122, 127, 128
extranuclear structure of, 16 ff.
number of electrons in, 11, 32, 33, 34
Atomic chemical behavior, 40
Atomic diameter, 6, 11, 36, 91, 105, 129, 130
Atomic dimensions, 91
Atomic gases and limit of elastic impact, 100

Atomic nuclei, 10 ff.

electrons in, 8

Atomic number, 11, 13, 32, 33, 34, 91
changed by emission of alpha and beta rays, 13

Atomic spectra and stable configurations, 25

Atomic spin and molecular heats, 83

Atomic structure, 13 ff., 17 ff., 91

Atomic weights, 13 ff., 27, 32, 33, 34, 57

Atoms, 1, 8, 10 ff., 16, 17 ff.

arrangement of electrons in, 18 ff.

electrical neutrality of, 16

electrons in outer structure of, 8

metastable, 118, 119, 122, 127, 128

multiply charged, 120

origin of concept of, 1

pictured on old Bohr theory, 31, 36, 37

Attachment of electrons, 8, 119, 123

Attractive forces, 46 ff., 92

Auger effect, 126

Average distance between molecular impacts, 2, 58, 64 ff., 67, 93, 131

Average molecular velocities, 73 ff.
ratio between, 74

Avogadro number, 57 ff., 133
accurate value of, 59
value of, 57

Avogadro's rule, 1, 2, 57 ff.

Axes, equipartition of energy along, 62

B

Balmer series, 24

Band, spectral, 44

Band spectrum, 42, 44 ff.

Behavior, chemical, 40 ff.
 Beryllium atom, structure of, 28
 Beta ray, change of atomic number by, 13
 Beta rays, 13, 128
 velocity of, 13
 Blue color of sky, 58
 Bohr orbits, 23 ff., 36, 37, 108
 Bohr's postulates, 19 ff.
 Bohr theory of spectral lines, 19 ff., 102
 Boltzmann constant, 59, 75, 132
 Boltzmann's calculation of distribution of velocities, 72
 Boron atom, structure of, 29
 Breakdown of dielectrics and surface adsorption, 55
 Bromine, molecular heat of, 82
 Brownian movements, 58

C

Carbon atom, structure of, 29
 Carboxyl group, structure of, 52
 Catalytic surfaces, 55
 Center of gravity in complex motion, 80
 Centrifugal forces, effect of, on molecules, 42
 CH_4 , structure of, 50
 Chance of a free path, 68 ff.
 Change of charge and relative ionizing potentials, 120
 Change of charge of alpha particles, 108, 114
 Characteristic equation, 7
 Charge, nuclear, and isotopes, 15
 of electron, 5, 132
 on nucleus, 11, 13, 32, 33, 34, 91
 on proton, 9
 Charges, transfer of, 118
 Chemical behavior, 40 ff.
 Chemical combinations, secondary, surface, 54
 Chemical reaction, by electron impact, 120
 ionization by, 128
 Chemical reactions by metastable atoms, 125

Cl_2 , molecular heat of, 82
 Classical electrodynamics, 6, 7, 18, 107
 CO , molecular structure of, 50
 Coherence, electronic, in atoms, 109
 Cohesive forces, 54
 Components, velocity, distributed along axes, 62, 75
 Computation of free paths, 70
 Concept of the free path, 65
 Condensation, latent heat of, 94
 of gases, 49, 94
 on surfaces, 54
 Conditions after excitation or ionization, 115 ff.
 Conservation of energy, law of, 2, 72, 93, 107
 Constant and multiple proportions, law of, 57
 Constant, Boltzmann, 59, 75, 132
 dielectric, 40, 51, 96
 Faraday, 58, 133
 Rydberg, 25
 Constants, important, 132, 133
 Continuous spectra, 119, 122
 Conversion factors important, 132, 133
 Coulomb's law, 5, 6, 10, 18
 Critical data, evaluation of free paths from, 70
 Critical potentials, 100, 102 ff.
 table of, 105, 106
 Crystal dissolves into ions, 51
 Crystal lattice, 51, 83, 95
 atomic heats of, 83
 ionic, 96
 Crystal lattices, specific heat at absolute zero, 83
 Crystals, formation of, 95

D

Dalton's law, 1, 2, 57
 Defect, mass, 14
 Degree of freedom, 79, 80, 85, 89
 energy per, 89
 Degrees of freedom, dormant, 85
 Degrees of freedom of motion, defined, 79

- Degrees of freedom of motion in different molecular types, 80
- Densities, vapor, 2
- Derivation, elementary, of mean free path, 64
- Detailed balancing, principle of, 89, 117
- Deviations from specific heat relations, 82
- Diameter, molecular, 42, 56, 92, 131
- Diameter of atom, 6, 11, 36, 91, 105, 129, 130
and ionization potential, 105
- Diameter of hydrogen molecule, 42
effective, 45 ff.
- Diameters of molecule, conditions dependent on, 56
- Diameters of nuclei, from scattering experiments, 7
- Diatomic gas, degrees of freedom of, 80
- Diatomic gases, molecular heat of, 80
- Dielectric constant, 40, 50, 51, 96
high, 40
temperature variation of, 51
- Dielectric constants, 51
- Dielectric properties of gases and liquids, 96
- Dielectrics, surface adsorption and breakdown of, 55
- Difference of path length for interference of light, 115
- Diffusion, evaluation of free paths from, 70
- Dimensions, atomic, 6, 11, 36, 91, 105, 129, 130
of electrons, 5, 91
of HCl molecule, 51
of proton, 9
physical and wave mechanical,
nearly equivalent, 7
- Dipole, electrical, 40, 46, 50, 51, 54, 55, 96
molecular, permanent, 51
- Dipole moments, 54
- Dipoles, 55
- Discharge phenomena not equilibrium processes, 90
- Disintegration, artificial, 9, 13, 98
protons from, 9
- Disruption of nuclei, spontaneous, 12
- Dissociation, and molecular velocity distribution, 77
by electron impact during vibration, 121
by impacts of the second class, 118
by metastable atoms, 125
of molecules, 43, 50, 55, 77, 86, 118, 120, 121, 125
by electron impact, 120 ff.
on surfaces, 55
- Dissociation energy, 50, 86
- Distribution law, and change of state, 95
and gradual appearance of quantum transition, 85
for molecular velocities, different forms of, 75 ff.
- Distribution of energies leads to gradual transitions, 85, 89, 93
- Distribution of energy, and condensation, 95
effect of on quantum transition, 89
- Distribution of free paths, 3, 67 ff.
importance of consideration in numerical problems, 69 ff.
proof of, 70
- Distribution of molecular velocities, 72 ff.
directly observed, 3
- Distribution of velocities, Maxwell's, 93
necessity of, 72
importance of in physical phenomena, 77
proven by thermionic emission, 78
- Doppler effect, 42, 44, 125
- Dormant degrees of freedom, 85
- Double electron jumps, 104
- Dual nature of ionization by massive particles, 108, 112
- Dulong and Petit's law, 2, 83
- Duration of emission and duration of excitation, 115
- Duration of emission from interference measurements, 115

- Duration of excited state, 43, 53, 115
 Duration of metastable state, 53,
 116
 Dynamical stability, 17
 molecular, 30
- E**
- Effect, Auger, 126
 Doppler, 125
 photoelectric, 123 ff., 128
 Einstein photoelectric equation, 123
 Elastic electron impacts, 90, 99
 Elastic impacts and velocity distribution, 72
 Electric behavior of gases, importance of mean free path in, 67
 Electrical breakdown of dielectric and ionization by positive ion, 113
 Electrical discharge phenomena, 71
 Electrical dipole moment, 40, 50, 51, 96
 Electrical force fields, 46 ff., 92
 Electrical moment, permanent, 50
 Electrical moments, induced, and permanent, 40, 46, 50, 51, 54, 55, 96
 Electrical neutrality, 16, 92
 of atoms, 16
 Electrical stability, 17
 Electricity, basis of all matter, 4
 operational nature of, 4
 positive and negative, 4
 ultimate nature of, 4
 Electrification, spray and frictional, 128
 Electrodynamic analysis of ionization, 106
 Electrodynamics, classical, 6, 7, 18, 107
 Electron, 4 ff.
 charge on, 5, 132
 early picture of, 4
 electrodynamical dimensions of, 6
 magnetic moment of, 7
 volt velocity of, 100, 132, 133
 work to pull out of metal, 123
 Electron attachment, 8, 119, 123
 Electron emission, and gas films, 55
 by metastable atoms, 118, 127
 by positive ion bombardment, 108, 127
 Electron energies in volts, 100, 132, 133
 Electron energy and photoelectric emission, 124
 Electron energy distribution and measurement of probabilities of ionization, 110
 Electron free paths, 111
 Electron groupings, changes with increasing atomic number, 31
 stable, table of, 39
 table of, 32, 33, 34
 Electron impact, and chemical reactions, 120
 dissociation of molecules by, 120
 probabilities of ionization by, 111
 probabilities of multiple ionization by, 112
 Electron impacts, elastic, 99
 fractional, energy loss in, 101
 Electron jumps, double, 104
 Electron levels or shells, 20, 39, 91
 Electron number and ionization potential, 105
 Electron orbits, changes in, 55
 necessity of, 18
 paradox of, 19
 Electron orbits and shells, hypothetical, 20
 Electron reflection and scattering experiments, 4
 Electron shells, energy of spin of, 86
 filling of, 36 ff.
 spin of, 84
 Electron shells or levels, subgroups in, 35
 Electron spin, 7
 Electron temperature high in discharge tube, 90
 Electronegative elements, 26, 40
 Electronic coherence in atoms, 109
 Electronic level, inner and *K*, X-rays, 34
 Electronic stable configurations, 38 ff.

- Electronic vibrations non-existent at room temperatures, 86
- Electrons, 4 ff., 91, 128
and ions, rare recombination of, 118
arrangement of in atoms, 18 ff.
elastic impact of, 90, 99
energy of, in discharge tube, 90
extranuclear, 8, 16 ff., 91
free, 8, 114, 123
disappearance of, 8, 123
in metals, 123
obscure pure temperature ionization, 114
in nucleus, 12
ionization by, 107 ff.
liberation of, 8, 102 ff., 106 ff.,
110 ff., 113, 114, 117, 118,
123 ff., 128
number of in atom, 11, 32, 33, 34
occurrence of, 8
of molecules and equipartition, 83
paired, 7, 28, 38, 41, 50, 91, 120
satellite, 11
secondary, 113
- Electropositive elements, 26, 40
- Elements, electropositive and electronegative, 26, 40
- Elliptic orbits, 20, 25
- Emission, duration of, from interference measurements, 115
of alpha and beta rays, change of atomic number by, 13
of light, 21, 24, 43
thermionic, 128
- Emission and excitation, duration of, 115
- Energies, involved in excitation, 86, 103
of dissociation, 86
of vibration, 86
- Energy, conservation of, 2, 72, 93, 107
law of, 2, 72
equipartition of, 62 ff.
law of, 78 ff.
- frequency of radiated, 21
in stable orbit, 21
kinetic, and ionization by positive ions, 127
- Energy of dissociation of molecules, 50, 86
of electrons, and photoelectric emission, 124
in discharge tube, 90
of spin of outer electron shells, 86
of translation of molecules, 62
per degree of freedom in equipartition, 79, 89
per degree of freedom of vibration, 83
radiation of, by accelerated charge, 19
to disrupt nucleus, 14
zero point, 92
- Energy distribution, in ionization, 103
in vibratory motion under equipartition, 82
- Energy distribution law, 76
- Energy equivalent of mass, 14
- Energy exchange between moving atomic structures rather free, 109
- Energy loss, computed, less than observed, 107
of fast particles calculated, 107
fractional, and electron impact, 101
- Energy losses, in polyatomic gases, 100
- Energy transfer, atomic, mechanical pictures inadequate, 99
- Energy transfers, probabilities of in second class impacts, 118
- Energy wall, high, surrounding nucleus, 12
- Equation, characteristic, 7
- Equilibrium, and velocity distribution, 72
prerequisite of equipartition, 89
stable, under inverse square law, 18
- Equilibrium temperature, 117
- Equipartition, 62 ff., 76, 78 ff., 89
and the quantum principle, 85
and vibration, 82
apparent failure of law of, 82
impropriety of simple application of, 84

Equipartition of energy, 62 ff.
 law of, 78 ff.
 per degree of freedom, 79
 Equipartition demands equilibrium, 89
 Evaporation and distribution of velocities, 78
 Excitation, duration of, 43, 53, 115
 energies involved in, 86
 of molecule effect on binding forces, 42
 Excitation and emission, duration of, 115
 Excitation and ionization, or multiple ionization, 104 ff.
 simultaneous, 104
 Excitation or ionization, conditions after, 115 ff.
 Excitation potentials, 103
 Excited atom, reactions of, 122
 Excited state, duration of, 43, 53, 115
 period of lingering in, 115
 Extranuclear electrons, 8, 16 ff., 91
 Extranuclear structure of atom, 16 ff.

F

Faraday constant, 58, 133
 Filling of electron shells, 36 ff.
 Fine structure of spectra, 44, 59
 Fluorescent radiation, 125
 Fluorine atom, structure of, 30
 Force fields, electrical, 5, 10, 46 ff., 92
 molecular, 46 ff., 92
 of solid surfaces, 54
 Forces, attractive and repulsive, 5, 10, 46, 54
 cohesive, 46, 54, 92
 molecular, repulsive and attractive, 46, 54, 92
 Formation of negative ions, 8, 123
 Forms, different, of distribution law, 75 ff.
 Fractional energy loss in electron impact, 101
 Free electrons, 8, 114, 123
 in metals, 123
 interference in temperature ionization, 114

Free path, mean, 2, 63 ff., 131
 Free paths, directly observed, 3
 distribution of, 67 ff.
 in mixed gases, 71
 Maxwell and Tait, 66
 significance of, as determined from different methods, 70
 Freedom, degrees of, defined, 79
 Frequency of radiated energy, 21 ff., 102, 105, 106, 107, 118, 125, 133
 Frictional electrification, 128

G

Gamma rays, 128
 Gas, instantaneous picture of, 94
 kinetic picture of a, 57 ff.
 Gas constant per mol, 59, 61, 75, 79, 81, 133
 Gas constant per molecule, 59, 75, 132
 Gas film, effect of on electron emission, 55, 127
 Gas molecules, velocity of, 60
 Gas only determines minimum sparking potential, 114
 Gaseous mixtures, free paths in, 71
 Gaseous reactions and atomic concept, 1
 Gases, condensation of, 49
 inert, 26
 kinetic theory of, 2, 57 ff.
 photoelectric processes leading to ionization in, 123 ff.
 sources of ionization in, 127 ff.
 sparking phenomena in, 55
 General considerations, 98, ff.
 Grouping, table of electron, 32, 33, 34

H

\hbar , Planck's, 7, 21, 42, 84, 123, 132
 Halides, organic structure of, 53
 Halogens, molecules of, 50
 HCl, structure of, 51
 HCl molecule, dimensions of, 51
 Heat, dissociation of molecules by, 43
 effect of on dielectric constant, 96
 mechanical equivalent of, 2, 62
 mechanical nature of, 2, 59 ff., 79 ff.

- Heat conduction, evaluation of free paths from, 70
 Heat motions of molecules, reality of, 3
 verified, 3, 97
 Heats, specific, 2, 62, 78 ff.
 Helium, molecules of, 53
 production of from alpha particles, 58
 spectra of, 25
 Helium atom, structure of, 28
 Helium nuclei are alpha rays, 12
 Historical, 1
 Homopolar molecules, 28, 41, 50
 "How," Newtonian, 99
 Hydrogen, absence of rotation in, at low temperatures, 87
 ortho- and para-, 9, 44
 spectra of, 24
 Hydrogen atom, structure of, 26
 Hydrogen atom nucleus is proton, 8
 Hydrogen molecule, 41 ff.
 Hydroxides, structure of, 52
- I
- Impact, electron, elastic, 99, 101 ff.
 probabilities of ionization by, 111
 triple, 119
 Impacts, inelastic, of the second class, 116 ff.
 Impacts of the second class, dissociation by, 118
 Important physical constants, 132, 133
 Imprisoned radiation, 125
 Inefficiency of ionization by positive ions, 113
 Inelastic impacts, of the second class, 116 ff.
 threshold value, 100 ff.
 Inert gases, 26
 stable electronic configurations of, 26, 39
 Inertia, moment of, in hydrogen, 87
 Infra-red absorption spectrum, 87
 Inner shells, ionization of, 105
 Instantaneous picture of a gas, 94
 Insulation, electrical, and ionization by positive ions, 112
 Intensity of photoelectric emission, 125
 Internal absorption of X-rays in atoms, 126
 Introduction, 1
 Inverse square law, 5, 6, 10, 18
 between alpha particles and nuclei, 10
 Ionic crystal lattice, 96
 Ionic mobilities and distribution of free paths, 69
 Ionization, after spark breakdown, high, 91
 by charged body, limiting velocity of, 108
 by electrons or alpha particles, 107
 by massive particles, dual nature of, 108, 112
 by moving particles, failure of theory analyzed, 108 ff.
 by neutral atoms and positive ions possible, 114
 by neutral atoms or molecules, 114
 by positive ions and temperature, 112 ff.
 by slow-moving positive ions, 108
 by temperature not cause of spark breakdown, 90
 energy distribution in, 103
 in gases, by photoelectric processes, 123
 sources of, 127 ff.
 mechanism of, 105 ff.
 multiple, or ionization and excitation, 104 ff.
 temperature, 114
 Ionization and excitation probabilities, 110 ff.
 Ionization or excitation, conditions after, 115 ff.
 Ionization phenomena, 98 ff.
 importance of walls in, 126
 Ionization potentials, 102, 103
 Ionization probabilities, difficulties in measuring, 110
 Ionizing potential of positive ions, 114

Ionizing potentials, relative, and change of charge, 120
 Ions, analogous to metastable atoms, 119
 and electrons, rare recombination of, 118
 atomic or molecular, 103
 dual nature of ionization by, 108, 112
 electrolytic, 40, 50
 in solution, 50
 number of, produced, 107
 recombination of, 96, 119
 solution of crystal into, 51
 transfer of charges by, 118
 Isotopes, 15, 57

J

Joule's law, 59 ff.
 Joule-Thomson effect, evaluation of free paths from, 70

K

K level or shell, 35
 K series, 25, 34, 35
 Kinetic energy, of molecules, and temperature, 61, 79 ff.
 of translation along one axis, 79
 Kinetic picture of a gas, 57 ff.
 Kinetic theory diameter of hydrogen molecule, 42
 Kinetic theory of gases, 2, 57 ff.

L

L level or shell, 35
 L series, 25, 34, 35
 Latent heat, of condensation, 94
 of fusion, 95
 Lattice, crystal, 51, 95
 formation of, 95
 Law, Coulomb's, 5, 6, 10, 18
 Dalton's, 1, 2, 57
 inverse square, 5, 6, 10, 18
 Joule's, 59 ff.
 Moseley's, 11
 of Dulong and Petit, 2, 83, 84
 of conservation of energy, 2, 72

Law of constant and multiple proportions, 57
 of detailed balancing, 89, 117
 of equipartition of energy, 78 ff.
 of thermodynamics, second, 2
 Laws of momentum and energy obeyed, 93, 107
 Layers, monomolecular, 54
 Levels, electron, 26, 35 ff., 91
 Liberation of electrons, 8, 102 ff., 104 ff., 106 ff., 110 ff., 113, 114, 117, 118, 123 ff., 128
 Light, absorption of, and photoionization, 124
 velocity of, 132
 Light emission, by positive rays, 115
 by salts in flames, 114
 Light emission not always an equilibrium process, 90
 Light radiation and orbits, 23 ff.
 Lithium atom, structure of, 28
 Line spectra, origin of, 24 ff.
 Liquid, nature of, 94
 Long periods, 36
 Loschmidt number, 3, 58 ff., 133

M

M level or shell, 35
 Magnetic fields, insignificant rôle of in ionization, 107
 Magnetic moment, of electron, 7 of proton, 9
 Mass, energy equivalent of, 14
 of atom of unit atomic weight, 9, 11, 133
 of electron, 4 ff., 132
 as function of velocity, 5
 of nucleus, 11
 of proton, 9
 Mass defect, 14
 Mass spectrograph, 15, 120
 Mass variation of proton with velocity, 9
 Masses, nuclear, and isotopes, 15
 Matter ultimately electrical, 4
 Maxwell-Boltzmann distribution law, 72 ff., 93

- Maxwell's free path, 66
 Mean free path, 2, 58, 63 ff., 67, 93,
 131
 calculation of, 64
 magnitudes of, 67, 131
 relative velocity correction for, 66
 Mean free paths, evaluation of, 70
 molecular, 131
 Measurement of Avogadro number,
 58
 Mechanical analogies, danger of, 3,
 99, 109
 Mechanical equivalent of heat, 2, 62
 Mechanical ether, 3
 Mechanical nature of heat, 2, 59 ff.,
 79 ff.
 Mechanical picture of ionization
 processes inadequate, 99
 Mechanics, Newtonian, 99
 quantum and wave, 3, 98, 121
 wave, 3, 99, 109
 Mechanism of ionization, 106 ff.
 Metallic elements have low ionization
 potentials, 105
 Metals, free electrons in, 8, 123
 Metastable atoms, 118, 119, 122, 127,
 128
 analogous to ions, 119
 electron emission by, 127
 ionization by, 128
 Metastable state, 53, 103, 116 ff., 117,
 125
 Methods for measurement of Avoga-
 dro number, 58
 Minimum sparking potential inde-
 pendent of electrode material,
 113
 Mobilities, ionic, and distribution of
 free paths, 69
 Molal heat capacity, at constant
 pressure in hydrogen, 88
 of solids at low temperatures, 88
 Molar volume, 57
 Molecular association, 53
 Molecular dimensions, 42, 56, 92, 129,
 131
 Molecular dissociation, 43, 50, 55, 77,
 86, 118, 120, 125
 Molecular dynamic stability, tetra-
 hedral, 30
 Molecular force fields, 46 ff., 92
 diagram of, 48
 Molecular forces, attractive and re-
 pulsive, 46, 92
 magnitude of, 49
 Molecular heat, and vibration, 83
 at constant pressure for different
 gases, 81
 at constant volume for different
 gases, 81
 in hydrogen at low temperatures,
 87
 of Cl_2 and Br_2 , 82
 of crystalline substances at low
 temperatures, 88
 of monatomic and diatomic gases,
 80
 of solid compounds, 89
 Molecular helium, formation of, 53
 Molecular impact, average distance
 between, 64 ff. *See also* Mean
 free path.
 Molecular motion quantitatively ver-
 ified, 97
 Molecular rotation, 42, 87
 Molecular rotation of hydrogen ceases
 at low temperatures, 43, 87
 Molecular scattering of sunlight, 58
 Molecular spectrum, 44 ff.
 Molecular structure, 41 ff.
 Molecular velocities, 71 ff.
 directly observed, 3
 distribution of, 73 ff.
 mean free paths and diameters,
 131
 Molecular velocity, 2, 3, 60 ff., 71 ff.,
 73 ff., 131
 variation with mass and tempera-
 ture, 60 ff.
 Molecular vibration, 43, 55, 82, 85,
 92, 121
 Molecule, hydrogen, 41 ff.
 shape of, 46
 Molecules, 57 ff., 92
 dissociation of, by electron impact,
 120 ff.

- Molecules, dissociation of, on surfaces, 55
 effect of centrifugal forces on, 42
 energy of dissociation of, 50, 86
 escaping from furnace, velocity of, 74
 number of, colliding in given distance, 69
 origin of concept of, 1
 radii of, table, 129, 130
 reality of heat motions of, 3, 97
 Moment of inertia of hydrogen, 87
 Moment of momentum, 42
 in orbits, 22
 Momentum and energy laws obeyed, 93, 107
 Momentum given electron in impact, 107
 Monatomic gas, atomic heat of, 80
 degrees of freedom in, 80
 Monomolecular layers, 54
 Moseley's law, 11
 Most probable velocity, 73
 Motion, electronic, and stability, 18
 Movement, Brownian, 58, 97
 Multiple ionization, by single electron impact, 104
 or ionization and excitation, 104 ff.
 probabilities of, 112
 Multiply charged atoms, 120
- N
- N_2 level or shell, 35
 N_2 , the molecular structure of, 50
 $NaCl$ molecules, 51
 Negative ions, formation of, 8, 119, 123
 Neon atom, structure of, 30
 Neutral atoms, ionization by, 112
 Neutral atoms or molecules, ionization by, 108, 112, 114
 Neutral molecule, ionization by, 108
 Neutrality, of atoms, electrical, 16
 electrical, 16, 92
 Newtonian mechanical analogue, 109
 Newtonian mechanics, 99
 Nitrogen, transmutation of, 13
 Nitrogen atom, structure of, 29
- Non-polar compounds, 28, 41, 50
 Non-polar molecules, 50
 Non-radiating orbits, 20 ff.
 Nuclear atom, 10
 Nuclear charge, 11, 13, 32, 33, 34, 91
 Nuclear disruption, emission of protons by, 9
 Nuclear structure, 11 ff.
 Nuclei, atomic, inviolate, 12, 98
 size of from scattering experiments, 7
 Nuclei of atoms, 10 ff.
 electrons in, 8
 Nucleus, 10 ff., 91
 high energy of, 12 ff., 91
 Nucleus of hydrogen atom is proton, 8
 Number, atomic, 11, 13, 32, 33, 34, 91
 Avogadro, 57 ff., 133
 Avogadro, Loschmidt, and atoms per cm^3 , 3, 57, 133
 Loschmidt, 3, 58 ff., 133
 of electrons in atom, 11, 13, 32, 33, 34, 91
 of molecules colliding in given distance, 69
 Number of molecules must be large in study of distribution, 72
 Number of possible electron orbits infinite, 19
 Numbers, quantum, 24, 103
- O
- O_2 level or shell, 35
 O_2 , molecular structure of, 50
 Occurrence of electrons, 8
 Octette, first complete, and L X-rays, 35
 Octettes, 3, 35, 38, 40, 50, 91, 120
 Octopole, 47
 Oil drop experiment, 97
 Operational character of electronic size, 5
 Operational nature of electricity, 4
 Orbit, stable, 21 ff.
 Orbits, electron, infinity of possible, 9
 electronic, necessity of, 18
 moment of momentum in, 22

Orbits, non-radiating, 20
 restricted, 20
 Orbita and shells of electrons, hypothetical, 20
 Origin of line spectra, 24 ff.
 Ortho- and para-hydrogen, 9, 44
 Ortho-hydrogen, 44
 Outer structure of atoms, electrons in, 8
 Oxygen atom, structure of, 30
 Oxygen seventeen, formation of, 13

P

P level or shell, 35
 Packing effect, nuclear, 14
 Paired electrons, 7, 28, 38, 41, 50, 91, 120
 Pairing of electrons, 7
 Palladium, free protons in, 9
 Para-hydrogen, 9, 44
 Paradox, of electron orbits, 19
 of molecular velocities, 63
 Periodic table, 11, 26, 27
 and atomic number, 11
 Periods, long, 36
 Permanent electrical moments, 50.
 See also Dipole.
 Permanent molecular dipoles, 51.
 See also Dipole.
 Perturbations, electronic, 45
 Phenomena, ionization, 98 ff.
 Photochemical reactions, 118, 126
 Photoelectric effect, 123 ff., 128
 Photoelectric emission, intensity of, 125
 Photoelectric equation of Einstein, 123
 Photoelectric processes leading to ionization in gases, 123 ff.
 Photoelectric threshold, 124
 Photoelectrons, secondary, 102
 Photoionization, and light absorption, 124
 probability of, 124
 Physical constants, important, 132, 133
 Physical dimensions, nearly equivalent to wave mechanical, 7

Physical phenomena, importance of molecular velocity distribution in, 77
 Physical size of electron, 5
 Picture, instantaneous, of a gas, 94
 Planck's h , 7, 21, 42, 84, 123, 132
 Planck's radiation law, 59, 84
 Polar compounds, 17, 26, 40, 51, 54, 96
 and ions in solution, 17
 Polar molecules, 50, 54, 96
 Polyatomic gas, molecular heat of, 80
 Polyatomic gases, energy losses in, 100
 Positive and negative electricity, 4
 Positive charges, 128
 Positive ion bombardment and electron emission, 127
 Positive ions, 108, 112 ff., 120, 122, 128
 and temperature, ionization by, 112 ff.
 difficulty in study of ionization by, 113
 electron emission by, and velocity, 127
 ionization by, 112 ff.
 essential in all electrical breakdown, 113
 inefficient, 113
 ionizing potential of, 114
 long-lived, 120, 122
 slow-moving, ionization by, 108
 Positive point, discharge from, 113
 Positive rays, light emission by, 115
 Postulates, Bohr's, 19 ff.
 Potential, ionizing, of positive ions, 114
 Potential and kinetic energies of electrons in orbits, 23
 Potentials, critical, 100, 102 ff.
 table of, 105, 106
 excitation, resonance and ionization, 103
 ionization, 102
 Pressure of a gas from kinetic theory, 59 ff.

Principle of detailed balancing, 89, 117
 Probabilities, of ionization and excitation, 110 ff.
 of ionization by positive ion at minimum potential, 115
 of multiple events in ionization, 104
 of multiple ionization, 112
 Probability, of energy transfer in impacts of the second class, 118
 of ionization by positive ions, 113
 of ionization, maximum, at ionizing potential, 110
 of photoionization, 124
 Proton spin, 9, 44
 Protons, 8 ff., 91, 128
 appearance of, 9
 free, 9
 in nucleus, 12
 ionization by, 112
 Pseudo-stable electron groups, 30, 35

Q

Q level or shell, 35
 Quadrupole, 47
 Quantitative verification of molecular motions, 3, 97
 Quantization of molecular rotation, 42, 87
 Quantum, constant of, action, 7, 21, 42, 84, 123, 132
 principle of, 82
 unit of, 84
 Quantum and wave mechanics, 3, 98, 121
 Quantum conditions, 63, 85, 106
 Quantum conditions rule atomic behavior, 21, 98
 Quantum limitation on equipartition, 89
 Quantum mechanics, 121
 Quantum numbers, 24, 103
 Quantum principle, and equipartition, 85
 and specific heats, 84 ff.
 Quantum restrictions, 92

Quantum theory, 3, 59. *See also* applications of theory under Quantum, above.

R

Radiation, fluorescent, 125
 imprisoned, 125
 in recombination, 118, 119
 Radiation law, Planck's, 59, 84
 Radiation of energy by accelerated charge, 19
 Radiation of light and orbits, 23 ff.
 Radiation potentials, 103
 Radii, of Bohr orbits, 23, 36
 of molecules, table of, 129, 130
 Radioactive elements, 38
 Radium, number of alpha particles given out by, 58
 rate of decay, 58
 Ratio of specific heats, for different gases, 81
 of Cl_2 and Br_2 , 82
 Ratios between various average molecular velocities, 74
 Reality of distribution of free paths, 70
 Reality of heat motions of molecules, 3, 97
 Recombination, of electrons and ions, rare, 118
 of ions, 119
 spectrum, 119
 Relative velocity correction for mean free path, 66
 Relativity, 3, 5, 9, 14
 theory of, 5
 Repulsive forces, 46 ff., 92
 Resonance potentials, 103
 Root mean square velocity, 73
 Rotation, equipartition in, 62
 molecular, 42, 55, 80, 89, 92
 Rotations absent in hydrogen at low temperatures, 43, 87
 Rule, Avogadro's, 1, 2, 57 ff.
 Rutherford, scattering experiments, 10
 Rydberg constant, 25
 Rydberg series, 24

- Satellite electrons, 11
 Scattering experiments, diameters of nuclei from, 7
 Scattering of alpha particles by nuclei, 10
 Second class, inelastic impacts of the, 116 ff.
 Second law of thermodynamics, 2
 Secondary chemical combinations, surface, 54
 Secondary electrons, 112
 Secondary photoelectrons, 102
 Series, Balmer, Rydberg and Lyman, 24
 Brackett, Fowler and Pickering, 25
 K and L , 25, 34, 35
 Shape of hydrogen molecule, 46
 Shells, K , L , M , N , O , P , Q , 35
 Significance of free paths from different methods, 70
 Simple derivation of value of mean free path, 65
 Single electron, dynamically unstable, 28
 Single electron impact and multiple ionization, 104
 Size, molecular, 42, 56, 92, 129, 131
 of electrical particle, interpretation of, 5
 of electron, physical, 5
 of particle, operational character of, 6
 of proton, 9
 Sky, blue color of, 58
 Sodium atom, structure of, 31
 Solids, electrical force fields of, 54
 Sources of ionization in gases, 127 ff.
 Spark breakdown, high energies after, 91
 Spark discharge mechanism and ionization by positive ions, 113
 Sparking phenomena in gases, 55
 Sparking potential influenced by surface films, 55
 Sparks, temperature ionization in, 90
 Specific heat, at constant pressure, 81
 at constant volume, 81
 Specific heat, ratio of, for different gases, 81
 Specific heat relations, deviation from, 82
 Specific heats, 2, 62, 78 ff., 84 ff.
 and quantum principle, 84 ff.
 Spectra, atomic, and stable configurations, 25
 continuous, 119, 122
 line, origin of, 24 ff.
 X-ray, 25
 Spectral lines, Bohr theory of, 22 ff., 102
 Spectrograph, mass, 15, 120
 Spectrum, many-lined, of hydrogen, 42
 molecular, 44 ff.
 Spherical molecules used in calculations, 72
 Spin, electron, 7
 proton, 9, 44
 Spontaneous disruption of nuclei, 12
 Spray electrification, 128
 Square root of average squared velocity, 73
 Stability, electrical and dynamical, 17 ff.
 of nucleus, 11, 12, 91
 Stable configurations, electronic, 38 ff.
 Stable electron groupings, table of, 39
 Stable electronic configurations of inert gases, 26, 39
 Stable equilibrium under inverse square law, 18
 Stable orbit, 21
 Stable orbits, radii of, and velocities in, 23
 State, metastable, 53, 103, 116 ff., 117, 125
 Structure, molecular, 41 ff.
 of atom, 13 ff., 17 ff., 91
 extranuclear, 16 ff.
 of nucleus, 11 ff.
 of water molecule, 51
 Structures of different atoms, 26 ff.

Subgroups in electron shells or levels, 30, 35
 Sublimation, 95
 Summary, 91 ff.
 Surface force fields of solids, 54
 Surfaces, condensation on, 54
 Swelling of molecules, 42

T

Table, of critical potentials, 105, 106
 of electron groupings, 32, 33, 34
 of stable electron groupings, 39
 Tait, free path, 66
 Temperature, absolute, 132
 and the kinetic energy of molecules, 61
 effect of on rotation of hydrogen, 87
 equilibrium, 117
 ionization, 114, 128
 ionization by positive ions and, 112 ff.
 ionization in sparks, 90
 of electrons and atoms in discharge tube, 90
 of glow discharge, 90
 Temperature and energy equivalent in volt velocity, 100, 133
 Temperature dissociation of molecules, 43
 Temperature variation, of dielectric constant, 51
 of molecular heats, 88
 Temperatures, effect of, on nuclei, 12
 Tetrahedral arrangement of atoms, 29, 30, 41, 50
 Tetrahedral symmetry, 41
 Theorem of equipartition, 62
 Theory of relativity, restricted, 5
 Thermionic effect and distribution of velocities, 78
 Thermionic emission, 128
 Thermodynamics, second law of, 2
 Three body problem in ionization, 107
 Threshold, photoelectric, 124
 Transfer of charges between ions and molecules, 118
 Transitions, gradual, due to distribution of velocities, 85, 89, 93

Translation, equipartition in, 62
 Translatory motion, 62, 89, 92
 Transmutation of nitrogen, 13
 Transport phenomena, evaluation of free paths from, 70
 Triple impact, 119

U

Ultimate nature of electricity, 4
 Ultra-violet light, photoelectric effect of, 123
 Ultraviolet radiations, origin of, 105
 Unit, of negative electricity, 5, 133
 of positive electricity, 9
 of quantum action, 7, 21, 42, 84, 122, 132
 Units of electricity, 4
 Unstable elements, 12, 38

V

Van der Waals' *b*, evaluation of free paths from, 70
 Van der Waals' equation, 58
 Vapor densities, 2
 Vapor pressure curve, expression of distribution of velocities, 78
 Velocities, molecular, 3, 71 ff., 131
 directly observed, 3
 distribution of, 73
 ratios between, averages, 74
 necessity of distribution of, among molecules, 72
 of electrons in Bohr orbits, 23
 of escaping molecules, 74
 of positive ions and electron emission by, 127
 Velocity, effect of on mass of electron, 5
 limiting, for ionization by charged body, 108
 molecular, 2, 3, 71 ff., 92, 131
 variation with mass and temperature, 60 ff.
 of electron, volt, 99 ff., 132
 of gas molecules, 60
 of light, 5, 7, 132
 of proton, mass variation with, 9
 variation of free path with, 71

- Velocity, volt, 100, 132
Velocity distribution law, different forms of, 75 ff.
Vibration, effect of on molecular heats, 83
 energy of, 86
 molecular, 43, 55, 82 ff., 85, 92, 121
Viscosity, evaluation of free paths from, 70
Volt velocity, 100, 132
 energy and temperature equivalent, 100, 132
Volume, molar, 57
 of a perfect gas, 133
- W
- Walls, importance of, in ionization phenomena, 126
Water, absorption of, in glass, 55
- Water molecule, structure of, 51
Wave mechanical and physical dimensions nearly equivalent, 7
Wave mechanics, 3, 4, 98, 99, 109, 116, 121
 experimental proof of, 4
Work function, 124
Work to remove electrons from metals, 8, 123
- X
- X-ray spectra, 25
X-rays, 31, 34, 35, 59, 105, 123, 128
 ionization by, 123
 origin of, 105
 wavelength of, 59
- Z
- Zero, absolute, no motions at, 92
Zero point energy, 92